Advanced electrocatalytic redox processes for environmental remediation of halogenated organic water pollutants

Madeleine K. Wilsey, a Teona Taseska, b Ziyi Meng, a Wanqing Yu b and Astrid M. Müller * abc

Halogenated organic compounds are widespread, and decades of heavy use have resulted in global bioaccumulation and contamination of the environment, including water sources. Here, we introduce the most common halogenated organic water pollutants, their classification by type of halogen (fluorine, chlorine, or bromine), important policies and regulations, main applications, and environmental and human health risks. Remediation techniques are outlined with particular emphasis on carbon–halogen bond strengths. Aqueous advanced redox processes are discussed, highlighting mechanistic details, including electrochemical oxidations and reductions of the water–oxygen system, and thermodynamic potentials, protonation states, and lifetimes of radicals and reactive oxygen species in aqueous electrolytes at different pH conditions. The state of the art of aqueous advanced redox processes for brominated, chlorinated, and fluorinated organic compounds is presented, along with reported mechanisms for aqueous destruction of select PFAS (per- and polyfluoroalkyl substances). Future research directions for aqueous electrocatalytic destruction of organohalogenes are identified, emphasizing the crucial need for developing a quantitative mechanistic understanding of degradation pathways, the improvement of analytical detection methods for organohalogenes and transient species during advanced redox processes, and the development of new catalysts and processes that are globally scalable.

Madeleine K. Wilsey completed her BS degree in chemistry and physics at Western Illinois University in 2019, where she conducted research under the supervision of Prof. Saisudha Mallur and Prof. J. Scott McConnell. After the completion of her undergraduate studies, Madeleine worked as an R&D intern at the company AP Lazer under the supervision of CEO Tong Li. Madeleine joined Prof. Astrid M. Müller’s group at the University of Rochester in summer 2020, and she is currently a PhD candidate investigating sustainable electrocatalysis for selective conversions of hydrocarbons into alcohols, using bimetallic nanocatalysts made by pulsed laser in liquids synthesis.

Teona Taseska, native of Ohrid, North Macedonia, came to the U.S. for her undergraduate education at the University of Rochester, where she is a rising senior in chemical engineering, clustering in Japanese. She has won the 2021 MLC Book Award for Japanese Language. She has been conducting undergraduate research in the lab of Prof. Astrid M. Müller since her sophomore year. Her research projects focus on opportunities for climate-friendly catalysis technologies to meet human needs on a global scale, hydrogen peroxide electroosynthesis, and the development of processes for the destruction of PFAS chemicals in aqueous systems, electrocatalyzed by laser-made nanomaterials.
Introduction

The industrial revolution led to unprecedented technological progress, human health, prosperity, wellbeing, and population growth, but it also caused climate change and environmental pollution on a global scale. Technological innovations in consumer goods, and pharmaceutical, agricultural, and industrial applications released large quantities of halogenated organic pollutants into the environment, including Earth’s waterways. Electrocatalytic technologies that remediate halogenated organic water pollutants can learn from other electrocatalysis fields and adapt analogue concepts, for example from water oxidation and oxygen reduction electrocatalysis, aqueous photoelectrochemical mechanisms, in situ and operando spectroscopies of electrocatalysts, and computational electrocatalyst design.

Halogenated organic water pollutants are hazardous for humans and animals. They are organic compounds that contain the halogen atoms fluorine, chlorine, or bromine, possess solubility in natural water, and are harmful to the environment. Halogenated organic compounds, also called organohalogens, are typically classified into different categories depending on their structure or chemical properties. Halogenated organic water pollutants include aliphatic or aromatic halogenated hydrocarbons. Common organohalogens are shown in Fig. 1. Organohalogens serve as solvents, coatings, degreasing agents, biocides, medical propellants, plasticizers, hydraulic and heat transfer fluids, chemical synthesis intermediates, refrigerants, coolants, and flame retardants.

Organohalogens possess exceptionally strong carbon–halogen bonds, leading to high heat resistance, low surface tension, high lipophilicity, and chemical inertness. Most organohalogens possess amphiphilic (ionic and neutral) properties and are xenobiotic, although natural organohalogens are known. Because of their thermodynamically strong covalent C–X (X = F, Cl, or Br) bonds, these compounds were initially considered nonmetabolizable and nontoxic, which turned out to be false, creating global human health risks and an urgent need for environmental remediation, particularly from water sources.

The discovery and manufacturing of organohalogens has led to revolutionary materials with high utility, such as non-stick Teflon cookware coatings, Rain-X water repellants, fire-retardant, water-proofing, and grease-resisting additives for electronics and microelectronics manufacturing. The widespread use of these chemicals has resulted in inadvertent or purposeful discharge into the environment. The high strength of carbon–halogen bonds inhibits biodegradation processes in nature, and leads to extended lifetimes and

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Ziyi Meng obtained his BSc in Polymer Materials and Engineering (2019) and MSc in Materials Science (2022) at Hubei University of Technology (China), where he conducted research in microbial modified mineral materials, advanced functional super elastic, and inorganic–organic composite proton exchange membrane fuel cells for extreme conditions under the supervision of Prof. Qingting Liu. In 2022, he enrolled at the University of Rochester as a PhD student in the Materials Science Program and joined the group of Prof. Astrid M. Müller to work on the degradation of per- and polyfluoroalkyl substances (PFAS), employing aqueous electrocatalysis and laser-made bimetallic nanomaterials.

Wanqing Yu

Wanqing Yu hails from Guangzhou, China, and came to the U.S. for her undergraduate education at the University of Rochester, where she obtained dual-major BS and BA degrees in chemical engineering and dance in 2023. At the University of Rochester, she conducted undergraduate research in the group of Prof. Astrid M. Müller, working on aqueous electrocatalytic defluorination of the PFAS chemical perfluorooctanoic acid, catalyzed by nanomaterials made by pulsed laser in liquids synthesis. In fall 2022, Wanqing received an Undergraduate Teaching Assistant Award in chemical engineering. Currently, Wanqing is a PhD student in chemical engineering at Georgia Institute of Technology.

Astrid M. Müller

Astrid M. Müller is an Assistant Professor of Chemical Engineering at the University of Rochester since 2018. Prof. Müller earned a PhD in Physical Chemistry for work on ultrafast reaction dynamics at the Max Planck Institute of Quantum Optics. Her postdoctoral work centred on developing a fundamental understanding of laser–matter interactions. Her independent research focuses on pulsed laser in liquids synthesis of mixed-metal nanomaterials with controlled structural and electronic properties. This uniquely positions Prof. Müller’s group to quantitatively understand how nanocatalysts and electrocatalytic mechanisms impact the performance of nanomaterials in sustainable energy, green chemistry, and aqueous PFAS destruction applications.
accumulation of chlorinated, brominated, and fluorinated organic compounds in the environment, animals and humans.\textsuperscript{20}

Policy regulations and restrictions regarding the manufacturing and use of halogenated organics have been instated on the national level and worldwide. For example, restrictions on the production of polychlorinated biphenyls (PCBs) began in 1970s, followed by international implementations through the Stockholm Convention in 2004, which banned the production of PCBs, aiming to phase out PCBs in use by 2025, and ensuring environmentally sound management by 2028.\textsuperscript{32} Limitations on brominated compounds started in 2009 when the Stockholm Convention listed polybrominated diphenyl ethers as new persistent organic pollutants and banned their production and use.\textsuperscript{33} Currently, five specific groups of brominated flame retardants are listed in the Stockholm Convention: hexabromobiphenyl, hexabromocyclododecane (HBCD), and the commercial polybrominated diphenyl ethers octabromodiphenyl ether (octaBDE), pentabromodiphenyl ether (pentaBDE), and decabromodiphenyl ether (decaBDE).\textsuperscript{33}

Additional policy efforts have been made to discontinue or limit the production and use of poly-fluorinated compounds. Significant New Use Rules were established in the U.S. to restrict the production and use of per- and polyfluoroalkyl substances (PFAS). The U.S. Environmental Protection Agency worked with leading chemical companies on a global phaseout of perfluorooctanoic acid (PFOA) through the 2010/2015 PFOA Stewardship Program to reduce emissions and residual content of PFAS.\textsuperscript{34} By 2009, perfluorooctane sulfonic acid (PFOS) and related compounds were listed under Annex B of the Stockholm Convention on Persistent Organic Pollutants.\textsuperscript{35} The U.S. Environmental Protection Agency’s notification levels for PFOA and PFOS are 5.1 and 6.5 ppt, respectively, and the response levels for PFOA and PFOS are 10 and 40 ppt, respectively.\textsuperscript{36,37}

Chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) are fully or partially halogenated hydrocarbons that are produced from methane, ethane, and propane. CFCs and HCFCs are nontoxic, non-flammable, and long-lived synthetic compounds that contain carbon, hydrogen, chlorine, and fluorine.\textsuperscript{38} Any production of CFCs was banned in 2010 through the Montreal Protocol to reduce CFC emissions into the atmosphere, where CFCs deplete stratospheric ozone.\textsuperscript{39}

Applications and health risks of halogenated organic water pollutants

Exposure to organohalogenes threatens human health.\textsuperscript{40–42} Resistance to biodegradation causes long lifetimes and accumulation of organohalogenes in the environment, together with global distribution via waterways.\textsuperscript{43} Bioaccumulation through food chains and direct uptake introduce organohalogenes into the human body, where they have been linked to Parkinson’s disease,\textsuperscript{44} harm in cognitive function and development, reproductive, hormonal, and metabolic processes, and increased risk for cancer.\textsuperscript{45,46,47} Specific applications and associated risks of chlorinated, brominated, and fluorinated organic compounds are detailed below.

**Chlorinated and brominated organic water pollutants.** Chlorinated and brominated organic water pollutants are harmful to human health and the environment.\textsuperscript{46,47} They accumulate in living organisms.\textsuperscript{46} Chlorinated organic compounds found uses in metal working fluids, lubricants, flame retardants, and plasticizers.\textsuperscript{48} Polybrominated diphenyl ethers
(PBDEs), polybrominated biphenyls (PBBs), tetrabromobisphenol-A (TBBPA), polybrominated phenols (PBPs), polychlordinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), polybrominated dibenzofurans and dibenzofurans (PBDD/Fs), and chlorinated polycyclic aromatic hydrocarbons (CIPAHs) are used in the manufacturing of electronic equipment and devices and remain in electronic waste (e-waste), creating serious pollution challenges in e-waste recycling.49

The high stability and environmental persistence of chlorinated organic compounds is attributable to the lipophilicity and high thermodynamic strength of C–Cl bonds.50,51 Common chlorinated organic water pollutants are polychlorinated dibenzodioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), PCBs, and chlorinated paraffins, whose global annual production exceeded 1 million metric tons in 2009,22 the year chlorinated compounds started to get restricted. Chlorinated alkanes are toxic: human exposure can harm the liver, kidneys, lungs, neurological systems, cardiovascular system, and immune system, and they have been linked to increased risk of cancer (Fig. 2).52 Although the production of PCBs has been phased out decades ago, 10 million tons of PCB-containing materials remain across the globe.32 PCBs accumulate in fat, liver, skin, and nerve tissues in humans (Fig. 2).29 Compounds produced by PCB detoxification in the liver have been linked to hormonal interference, reproductive,53,54 metabolic,55 and neurological dysfunction,56 and cancer (Fig. 2).57 The extent of toxicity depends on the chemical structure of chlorinated organic compounds and particularly the position of chlorine atoms on phenyl rings, with the highest toxicity observed for chlorine in meta and para positions.28 Dioxins have been linked to similar reproductive, neurological, and carcinogenic issues as PCBs.20 Chlorinated organic compounds often originate in small organisms and transfer through food chains to accumulate in higher-order species in large doses.20

Most brominated organic water pollutants are commonly known as brominated flame retardants (BFRs), which are used across many industries to inhibit or suppress combustion processes. BFRs are often found in plastics, textiles, electronic circuitry, and building materials.49,59 The utility of BFRs has led to a growing market with a global market size of 2.14 billion USD in 2022 and a compound annual growth rate of 5.7%.60 BFRs are lipophilic and bioaccumulate if leached from products, during manufacturing, or during incineration.61 Brominated, like chlorinated, organic pollutants accumulate in the environment and threaten human health by build-up in lipid tissues.20 Specific health effects caused by BFRs are less understood than those of PCBs. BFRs have been linked to interfering with nerve development in fetuses and newborns, and harming infant cognitive function (Fig. 2).60,62

Fluorinated organic water pollutants. Organofluorine compounds have widely been used in industry because of high heat resistance, low surface friction, and chemical inertness.63 The exceptional utility, concomitant broad use, and chemical resistance of materials that contain C–F motifs, together with detrimental human health effects have led to concerns about accumulation of fluorinated chemicals; specific health and environmental effects are detailed below, organized by class of fluorinated organic pollutants.

Partially fluorinated solvents. Partially fluorinated solvents are commonly utilized in pharmaceuticals, as surfactants, and in energy devices.64–66 Partially fluorinated solvents are pollutants because they contribute to ozone depletion, global warming, bioaccumulation, and toxicity, especially in drinking water supplies,67 leading to elevated risk of thyroid disease, high cholesterol, ulcerative colitis, kidney cancer, testicular cancer, and pregnancy-induced hypertension (Fig. 2).68

Chlorofluorocarbons and hydrochlorofluorocarbons. The most widely known representatives of CFCs and HCFCs are Freons. Trichlorofluoromethane (also known as Freon-11, CFC-11, or R-11) and dichlorodifluoromethane (also known as Freon-12, CFC-12, or R-12) are primarily used as coolants in air conditioning and refrigeration applications, blowing agents in foams, insulation, packing materials, propellants in aerosol cans, and solvents.69 Chlorotrifluoromethane (also known as Freon-13, CFC-13, or R-13) is predominantly employed in the manufacturing of semiconductor chips, in vapor degreasing, and in cold immersion cleaning of microelectronic components, or as a solvent in procedures for surface cleaning in the electronics industry.60 Chlorodifluoromethane (HCFC-22), 1-chloro-1,1-difluoroethane (HCFC-142b), and 1,1-dichloro-1-fluoroethane (HCFC-141b) are mainly used as refrigerants and blowing agents in foams.70 CFCs are acutely toxic upon inhalation; adverse effects include central nervous system depression, asphyxia, and cardiac arrhythmia (Fig. 2).71 HCFCs are more flammable and more susceptible to decomposition during use than CFCs, by which toxic byproducts can be formed.72,73 Hydrofluorocarbons (HFCs) gradually replace CFCs and HCFCs because they are generally less toxic than HCFCs for aquatic life, terrestrial plants, and mammals, including humans.73 The flammability of HFCs is higher than that of CFCs and HCFCs.74 HFCs possess very low solubility in water, making them insignificant water pollutants.73

Per- and polyfluorinated substances (PFAS). PFAS are heat-, water-, and oil-resistant synthetic chemicals that are widely

![Fig. 2](human-health-risks-upon-exposure-to-halogenated-organic-water-pollutants.png)
used in consumer, commercial, and industrial products, from aerospace to food production. Fluoropolymer coatings can repel water and oil, and resist thermal, chemical and biological decomposition. Decades of heavy use have resulted in bioaccumulation and contamination of water, soil, animals, and people all over the world. PFAS accumulation has even been observed in Antarctica. For example, the PFAS chemical PFOS bioaccumulates in fish that is trapped by bile acid transporters, resulting in a half life of 7.1 years in humans. PFAS exposure is harmful to human health. The extreme chemical stability of PFAS arises from numerous C–F bonds, which is beneficial for the durability of products, but problematic for the environment and ultimately human health, as PFAS resist biodegradation.

PFAS have been identified in ground water, surface water, drinking water, soil, indoor air, dietary sources, manufacturing locations, and wastewater treatment plants, as well as in human blood, serum, milk, urine, and placenta tissue. For example, the PFAS chemical PFOS bioaccumulates in fish that consumes humans, making such fish a source of human PFAS exposure. Human PFAS exposure can additionally occur via dermal contact because PFAS can be taken up from oil- and water-resistant non-stick coatings on cookware and paper food packaging materials. Inhalation of indoor air and household dust is another route for human PFAS uptake.

Human exposure to PFAS causes reproductive and immune system harm, increased risk of non-Hodgkin’s lymphoma and leukemia, testicular, prostate, breast, liver, and ovarian cancers, decreased vaccine response, increased risk of asthma in adolescents, increased risk of diabetes and hypertension in women, developmental delays in children, changes in liver enzymes, endocrine disruption, and increased cholesterol levels and/or risk of obesity; in unborn children, delayed mammary gland development, reduced response to vaccines, and lower birth weight have been observed. PFAS also pose ecological risks through bioaccumulation, food chains, and toxicity in terrestrial and aquatic wildlife.

Remediation techniques for halogenated organic water pollutants

Maximum contaminant limits in water in the U.S. are set by the U.S. Environmental Protection Agency and published in the National Primary Drinking Water Regulations. For most chlorinated, brominated, and fluorinated organic pollutants, the allowable contamination threshold is on the order of parts per billion (ppb) or parts per trillion (ppt), depending on the compound and associated risks. To achieve safe levels, water remediation techniques are needed for effective removal and destruction of pollutants. Halogenated organic pollutants have a particularly high resistance against degradation because of their strong carbon–halogen bonds. As a result, only a few destruction techniques for complete mineralization of halogenated organic water pollutants have been commercialized, and the field is a very active research area. Several separation techniques have found commercial use to remove halogenated pollutants from water sources; separation only concentrates pollutants, after which disposal by destruction is necessary.

Concentration vs. destruction techniques

Organohalogen concentrations differ vastly across water sources and mainly depend on the distance from the location of pollutant discharge. For example, PFAS concentrations in drinking water range from 26 to 5200 ng L⁻¹. For illustration, the lower limit corresponds to approximately one drop in an Olympic swimming pool full of water. Freshwater sources are typically contaminated with PFAS at levels on the order of hundreds of nanograms per liter, whereas concentrations in marine water are at tens of nanograms per liter.

Concentration techniques. Halogenated organic compounds have been separated from water by nitrifying fluidized-bed biomass or by distillation, taking advantage of volatility differences between organohalogenes and water before discharging the water into sewage systems. Adsorption and reverse osmosis separation methods have been described to concentrate chlorinated and brominated organic pollutants from dilute natural water sources.

Adsorption techniques. Adsorption utilizes physical or chemical interactions between the surface of a solid (adsorbent) and a solute (adsorbate) to remove pollutants from water sources. In contrast, absorbents are porous materials that take up matter into spaces within and throughout the material. Adsorbable organic halogens are removed from water by adsorption methods, such as PuF/e/a metal bimetallic particles to treat activated sludge of chemical dyestuff wastewater. Granular activated carbon and powdered activated carbon are the most frequently used adsorbents, but activated alumina and zeolites have also been employed. Two common chlorinated groundwater pollutants, tetrachloroethylene and trichloroethylene, have shown significant adsorption on granular activated carbon. Likewise, absorbent materials that are capable of removing brominated water pollutants include metal organic frameworks, biochar, and microplastics.

Reverse osmosis. Reverse osmosis is a separation technique that passes water through a semi-permeable membrane that discharges a treated stream (permeate) and a rejection stream (concentrate). Reverse osmosis decreased the concentration of 2,3,7,8-substituted polychlorinated dibenzo-p-dioxins (PCDD), dibenzoarufans (PCDFs), and dioxin-like PCBs in water.

Destruction techniques. Destruction of organohalogenes is preferable over standalone separation. Separation pre-treatment procedures are often used to increase organohalogen concentrations in water to enhance degradation efficiency by overcoming substrate mass transport limitations that are inherent with dilute solutions. Destruction techniques cleave carbon-halogen bonds to produce carbon chemicals that are less harmful than organohalogenes, ultimately CO₂, and halogen-containing non-water-soluble mineral-like solids, which is called mineralization. Reported destruction methods for pollutant...
The bond dissociation energy values, which are a measure for thermodynamic bond strength, show that halogen atoms with higher electronegativity form stronger bonds to carbon atoms (Table 1). Fluorine is the most electronegative element in the periodic table and ergo C–F bonds are the strongest covalent bonds known in organic chemistry. In general, electronegativity of halogens follows F > Cl > Br, and likewise the trend in bond strengths follows C–F > C–Cl > C–Br. The C–F bond dissociation energies in PFAS depend on the extent of fluorination of carbon atoms, the position of C–F bonds, and the nature of the head group in the molecule (Fig. 3).

In contrast, in chlorinated and brominated organic compounds, dissociation energies of C–X (X = Cl or Br) bonds depend on the degree of substitution at the carbon of the C–X bond. Thus, the strongest C–X bonds of chlorinated and brominated compounds are found in halogenated phenyls.124

**Threshold limit values and response levels of common halogenated organic water pollutants**

Threshold limit values (TLVs) serve as important benchmarks for monitoring workplace exposure. These values denote permissible airborne concentrations of chemical substances that the majority of workers can encounter in a repetitive manner throughout their career span, without detrimental health consequences. The American Conference of Governmental Industrial Hygienists (ACGIH) formulates TLV-time-weighted averages (TLV-TWAs) to safeguard against prolonged exposures, as well as short-term exposure limits to shield against sudden spikes in exposure. It is important to note that TLVs are not designed to establish a rigid demarcation between safe and hazardous exposures. Instead, their primary objective is to safeguard workers from potential health impacts.125 The notification level is the concentration of a hazardous substance in the environment, above which specific actions or notifications are required. Notification levels are often used to assess water pollutants because they represent human health-based advisory levels for chemicals in drinking water, which lack maximum contaminant levels.126 Human health-based advisory levels establish the contaminant concentration in drinking water, below which no adverse health effects and/or aesthetic impacts are expected during specific periods of exposure.127 Actions might include reporting the presence of the substance to regulatory authorities or taking steps to mitigate the exposure or contamination. Notification levels are typically set by regulatory agencies and are designed to alert relevant parties when a certain level of contamination has been reached. In contrast, the response level represents a concentration of a hazardous substance in the environment that triggers specific actions or interventions to mitigate risks and protect human health or the ecosystem. Response levels are set to guide the appropriate measures to be taken when contamination reaches a certain level. These measures might include evacuation, containment, or clean-up, to prevent further exposure or harm.126 TLVs and notification levels of common halogenated organic water pollutants that are discussed in this article are in Table 2.

**Destructive remediation of chlorinated and brominated organic water pollutants**

Destructive methods are necessary to treat waste streams or sludges after concentration of target pollutants by separations. Chlorinated and brominated organic pollutants can be destroyed by incineration, non-thermal plasma discharge, γ-irradiation, biological, catalytic, photolytic, photocatalytic, or photochemical processes.

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**Table 1** Bond dissociation energies for different binding motifs of halogens X for common organohalogenes. Energy ranges originate from different bond dissociation energies depending on the position of the F atom within the molecule. PFOA, perfluorooctanoic acid; PFOS, perfluorooctane sulfonic acid. From ref. 116–123.

<table>
<thead>
<tr>
<th>X</th>
<th>R–X</th>
<th>Bond dissociation energy (kJ mol⁻¹)</th>
</tr>
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<tbody>
<tr>
<td>F</td>
<td>GenX–F</td>
<td>536.0</td>
</tr>
<tr>
<td></td>
<td>HF–F</td>
<td>534.7</td>
</tr>
<tr>
<td></td>
<td>H₂C₂–F</td>
<td>526.0</td>
</tr>
<tr>
<td></td>
<td>H₂FC–F</td>
<td>499.2</td>
</tr>
<tr>
<td></td>
<td>HO₂C₂F₂–F (PFOA)</td>
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<tr>
<td></td>
<td>H₂C–F</td>
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<tr>
<td></td>
<td>O₂F₂C₂F₆–F (PFOS)</td>
<td>415.6–461.9</td>
</tr>
<tr>
<td>Cl</td>
<td>H₂C₂–Cl</td>
<td>400.0</td>
</tr>
<tr>
<td></td>
<td>(H₂C)₂C–Cl</td>
<td>359.4</td>
</tr>
<tr>
<td></td>
<td>H₂CH₂CH₂C–Cl</td>
<td>356.9</td>
</tr>
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<td></td>
<td>H₂CH₂C–Cl</td>
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<tr>
<td></td>
<td>H₂C–Cl</td>
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<tr>
<td></td>
<td>H₂ClC–Cl</td>
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</tr>
<tr>
<td></td>
<td>HCl(C–Cl)</td>
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</tr>
<tr>
<td></td>
<td>H₂C₂H₂C–Cl</td>
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</tr>
<tr>
<td>Br</td>
<td>H₂C₂–Br</td>
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</tr>
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<td></td>
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</tr>
<tr>
<td></td>
<td>H₂C(H₂C)₂–Br</td>
<td>303.3</td>
</tr>
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<td></td>
<td>H₂C(H₂C)–Br</td>
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</tr>
<tr>
<td></td>
<td>H₂C–Br</td>
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<tr>
<td></td>
<td>H₂BrC–Br</td>
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<tr>
<td></td>
<td>HBr(C–Br)</td>
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<tr>
<td></td>
<td>H₂C₂H₂C–Br</td>
<td>248.5</td>
</tr>
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</table>

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**Fig. 3** Bond dissociation energies in kJ mol⁻¹ of C–F bonds by position in perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS). From ref. 122 and 123.
Table 2. Notification levels, response averages, and threshold limit values (TLVs) for common halogenated organic water pollutants in water unless otherwise noted; TLVs are for exposure averaged over an 8-hour work shift unless otherwise noted. Abbreviations of chemicals (in order of appearance): PFBA, perfluorobutanoic acid; GenX, hexafluoropropylene oxide dimer acid; PFDA, perfluorodecanoic acid; PFOS, perfluorooctane sulfonic acid; PFOA, perfluorooctanoic acid; Freon-11, trichlorofluoromethane; Freon-12, dichlorodifluoromethane; Freon-13, chlorotrifluoromethane; HCFC-22, chlorodifluoromethane; HCFC-142b, chloro-1,1-difluoroethane; HCFC-141b, 1,1-dichloro-1-fluoroethane; VC, vinyl chloride; DCE, 1,2-dichloroethene; PERC, tetrachloroethene; TCE, trichloroethene; 2,3,7,8-TCDD, 2,3,7,8-tetrachlorodibenzodioxin; PCB-47, 2,2',4,4',5,5'-hexachlorobiphenyl; PCB-77, 1,2-dichloro-4-(3,4-dichlorophenyl)benzene; BDE-47, 2,2',4,4',5,5',6,6'-heptabromobiphenyl; TBBPA, tetrabromobisphenol-A. Units: ppm (mg L⁻¹), ppb (µg L⁻¹), ppt (ng L⁻¹), ppq (pg L⁻¹).

<table>
<thead>
<tr>
<th>Class</th>
<th>Compound</th>
<th>Notification level</th>
<th>Response level</th>
<th>Ref.</th>
<th>Threshold limit value</th>
<th>Ref.</th>
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<tr>
<td>Fluorinated</td>
<td>PFBA</td>
<td>100 ppt</td>
<td>1000 ppt</td>
<td>128</td>
<td>5 ppt</td>
<td>129</td>
</tr>
<tr>
<td></td>
<td>GenX</td>
<td>30 ppt</td>
<td>300 ppt</td>
<td>128</td>
<td>5 ppt</td>
<td>129</td>
</tr>
<tr>
<td></td>
<td>PFDA</td>
<td>20 ppt</td>
<td>—</td>
<td>130</td>
<td>3 ppt</td>
<td>131</td>
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<tr>
<td></td>
<td>PFOS</td>
<td>6.5 ppt</td>
<td>40 ppt</td>
<td>131</td>
<td>4 ppt</td>
<td>131</td>
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<tr>
<td></td>
<td>PFOA</td>
<td>5.1 ppt</td>
<td>10 ppt</td>
<td>131</td>
<td>4 ppt</td>
<td>131</td>
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<td></td>
<td>PFHxS</td>
<td>3 ppt</td>
<td>20 ppt</td>
<td>131</td>
<td>3 ppt</td>
<td>131</td>
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<tr>
<td>Fluorinated−chlorinated</td>
<td>Freon-11</td>
<td>5 ppb</td>
<td>150 ppb</td>
<td>131</td>
<td>1000 ppm (airborne)</td>
<td>132</td>
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<tr>
<td></td>
<td>Freon-12</td>
<td>1 ppm</td>
<td>10 ppm</td>
<td>131</td>
<td>1000 ppm (airborne)</td>
<td>132</td>
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<tr>
<td></td>
<td>Freon-13</td>
<td>—</td>
<td>3000 ppm</td>
<td>135</td>
<td>Not established</td>
<td>136</td>
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<tr>
<td>Chlorinated</td>
<td>VC</td>
<td>2 ppb</td>
<td>2 ppb</td>
<td>140</td>
<td>1 ppb (airborne)</td>
<td>142</td>
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<td>DCE</td>
<td>500 ppb</td>
<td>500 ppb</td>
<td>131</td>
<td>2 ppm (airborne)</td>
<td>143</td>
</tr>
<tr>
<td></td>
<td>PERC</td>
<td>500 ppb</td>
<td>500 ppb</td>
<td>131</td>
<td>25 ppm (airborne)</td>
<td>144</td>
</tr>
<tr>
<td></td>
<td>TCE</td>
<td>5 ppb</td>
<td>500 ppb</td>
<td>131</td>
<td>10 ppm (airborne)</td>
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</tr>
<tr>
<td></td>
<td>— 2</td>
<td>100 ppb (based on water)</td>
<td>— 146</td>
<td>Not established</td>
<td>146 and 147</td>
<td></td>
</tr>
<tr>
<td>Brominated</td>
<td>BDE-47</td>
<td>—</td>
<td>24 ppb</td>
<td>150</td>
<td>50 mg kg⁻¹ body weight per day</td>
<td>151</td>
</tr>
<tr>
<td></td>
<td>BDE-207</td>
<td>—</td>
<td>—</td>
<td>50 mg kg⁻¹ body weight per day</td>
<td>151</td>
<td></td>
</tr>
<tr>
<td></td>
<td>TBP</td>
<td>—</td>
<td>—</td>
<td>Not established</td>
<td>152</td>
<td></td>
</tr>
<tr>
<td></td>
<td>HBCD</td>
<td>—</td>
<td>—</td>
<td>100 mg kg⁻¹ body weight per day</td>
<td>153</td>
<td></td>
</tr>
<tr>
<td></td>
<td>TBBPA</td>
<td>—</td>
<td>15 ppb</td>
<td>154</td>
<td>10 ppb</td>
<td>155</td>
</tr>
</tbody>
</table>

* Massachusetts drinking water maximum contaminant levels, PFDA combined with other PFAS.† California drinking water standards.

**Incineration.** Incineration has been widely used to reduce the volume, potential infectious properties, and potential toxicity of waste.¹⁶⁰ This process burns the hazardous waste to carbon dioxide and water vapor, while also producing byproducts that are released as exhaust gas or remain as solid ash or soot.¹⁶⁰ Incineration has the advantage that large amounts of waste can be treated in a short period of time,¹⁶⁰ while additionally offering the possibility of providing heat energy in the form of steam or hot water.¹⁶¹ Incineration also has the advantage that the efficiency of ρ-radiation relies on the extent to which the radiation source has decayed, as that determines the deliverable dose. Non-thermal plasma has the advantage that the efficiency relies on electromagnetic generation of particles, which does not decay over time; however, its high energy demand creates inherent barriers for global use.¹⁶³ Non-thermal plasma discharge has been described for the degradation of PCB-77 (80% within 2 min) using a dielectric barrier discharge non-thermal plasma,¹⁵⁸ whereas PCB-47 was degraded by 70% within 60 min using pulsed corona discharge.¹⁶⁵ PCBs can also be decomposed with ionizing radiation in aqueous micellar solutions.¹⁶⁶ However, γ-radiation hazards originating from the required ⁶⁰Co γ-irradiation source must be mitigated.¹⁶⁶

**Non-thermal plasma and γ-irradiation.** Non-thermal plasma treatment utilizes high-voltage electrical pulses to generate a corona discharge that excites electrons in the air to produce singlet oxygen, which reacts with water to generate ozone and hydroxyl radicals for pollutant destruction.¹⁶² Gamma-irradiation utilizes γ-rays with sufficient energy, often from a ⁶⁰Co source, to ionize atoms, resulting in cleavage of molecular bonds, such as water, to create reactive radical species for pollutant destruction.¹⁶² In addition to the inherent safety precautions and high-risk handling procedures of γ-rays, the efficiency of γ-irradiation relies on the extent to which the radiation source has decayed, as that determines the deliverable dose. Non-thermal plasma has the advantage that the efficiency relies on electromagnetic generation of particles, which does not decay over time; however, its high energy demand creates inherent barriers for global use.¹⁶³ Non-thermal plasma discharge has been described for the degradation of PCB-77 (80% within 2 min) using a dielectric barrier discharge non-thermal plasma,¹⁵⁸ whereas PCB-47 was degraded by 70% within 60 min using pulsed corona discharge.¹⁶⁵ PCBs can also be decomposed with ionizing radiation in aqueous micellar solutions.¹⁶⁶ However, γ-radiation hazards originating from the required ⁶⁰Co γ-irradiation source must be mitigated.¹⁶⁶

**Chemical and biological techniques.** Chemical and biological techniques make use of chemicals or microorganisms, respectively, to break down organic matter. Chemical processes are attractive destruction methods due to their simple operation; however, stoichiometric use of chemicals and associated production of sludge create large amounts of chemical waste, contributing to operational cost and complexity of separation.¹⁶⁸ Biological techniques have the advantage of...
being self-sustaining processes, which result in less cost compared to methods requiring chemical additives or extensive maintenance. Nevertheless, biological processes require extended time for microbial growth, and the performance can suffer from inherent environmental factors, such as temperature or water composition.\textsuperscript{169,170} Catalytic or oxidative processes have been reported for breakdown of chlorinated and brominated organic pollutants.\textsuperscript{171,172} Biological processes have been applied to treat brominated water pollutants, such as anaerobic–aerobic processes for microbial degradation of tetrabromobisphenol-A.\textsuperscript{173}

**Electrochemical techniques.** Electrochemical techniques utilize electrical energy to induce the mineralization of dissolved contaminants in water. Electrochemical systems offer many advantages, including operation at ambient temperature and pressure, no required auxiliary chemicals, and small footprint, making it an attractive technique for delocalized water treatment.\textsuperscript{174} However, electrochemical technologies must be improved with regard to toxic by-products that result from inefficient mineralization, and with respect to electrode costs to enable adoption on an industrial scale.\textsuperscript{174} Chlorinated and brominated organic water pollutants have been degraded by electrochemical processes.\textsuperscript{25,175,176} Electrooxidative\textsuperscript{176,177} and electroreductive\textsuperscript{19,178,179} methods were used via direct electrocatalytic electron transfer or indirect interactions with electrochemically produced highly reactive transient species. We note that the production of toxic liquid bromine or chlorine gas is an inherent obstacle in electrooxidations of chlorinated or brominated water pollutants.\textsuperscript{110,180–182}

**Photo-assisted techniques.** Photo processes and photo-assisted techniques utilize light absorption by molecules to directly dissociate target species or indirectly create reactive radical species in solution that carry out the degradation. Photo processes have several advantages, including operation at ambient temperature and pressure, low energy requirement, and no need for additional chemicals.\textsuperscript{27} Nevertheless, current photo processes lack degradation and mineralization efficiency, resulting in by-product formation.\textsuperscript{27} Methods involving illumination with light in the visible to vacuum ultraviolet range, such as direct photolysis or indirect photocatalytic and photochemical processes have been utilized for chlorinated and brominated pollutant mineralization.\textsuperscript{183,184}

**Sonolysis.** Sonolysis utilizes the compression and expansion cycles of ultrasound waves that produce hot spots with high temperatures (approximately 5000 K) and pressures (approximately 1000 atm), due to cavitation bubble collapse.\textsuperscript{185} In these hot spots, molecular bonds are cleaved directly through photolysis or indirectly through reactions with reactive radical species produced via photolysis.\textsuperscript{185} Sonolysis is advantageous because no chemical additives are required and it is a simple process;\textsuperscript{186,187} however, the localized production of high concentrations of reactive radical species is limited by recombination leading to inefficient degradation.\textsuperscript{188} Direct pollutant destruction via sonolysis has been applied to remediate chlorinated and brominated water pollutants.\textsuperscript{185,189–191} To enhance the degradation efficiency of sonolysis processes, auxiliary chemicals have been added to solutions that contained chlorinated or brominated pollutants.\textsuperscript{189,192}

**Recent progress in the destruction of chlorinated organic water pollutants**

**PCBs.** Multiple PCBs were degraded via a combination of adsorption, photodegradation, and heterogeneous Fenton oxidation reactions, using a multifunctional magnetic β-cyclodextrin/graphitic carbon nitride catalyst (Fe\textsubscript{3}O\textsubscript{4}@β-CD/g-C\textsubscript{3}N\textsubscript{4}), with a degradation efficiency for different PCBs in wastewater ranging from 77% to 98%.\textsuperscript{193} PCBs from transformer oil were photocatalytically degraded using carboxymethyl-β-cyclodextrin modified Fe\textsubscript{3}O\textsubscript{4}/TiO\textsubscript{2x}, with a degradation rate of PCBs by 83% after 16 minutes.\textsuperscript{194} Dielectric barrier discharge non-thermal plasma degraded PCB77 in aqueous solution with a removal efficiency of PCB77 of 80% with helium as discharging gas and approximately 75% with oxygen as discharging gas.\textsuperscript{158}

**Dioxins.** Dielectric barrier discharge in a lab-scale reactor degraded 2,3,7,8-TCDD in fly ash with a removal efficiency of 92%; this process was also used for degradation of other PCDD/Fs-containing fly ash, whose degradation efficiency depended on input energy and discharge time.\textsuperscript{195} Another reported method to degrade 2,3,7,8-TCDD is use of extracellular fungal ligninolytic enzymes that were made of laccase enzymes. Ligninolytic fungus *Rigidoporus umbrinus* sp. FMD21 degraded 2,3,7,8-TCDD by 77.4% in 36 days and produced 3,4-dichlorophenol.\textsuperscript{196}

**Tetrachloroethylene (perchloroethylene, PCE).** Degradation of PCE occurred under aerobic conditions using *Sphingopyxis umbrariensis* bacteria in a gas-recycling fixed-bed bioreactor.\textsuperscript{197} This process was more efficient with lower concentrations of PCE and achieved complete degradation of PCE in 25 hours.\textsuperscript{197} PCE degradation using cobalt-mediated electroscrubbing with boron-doped diamond (BDD) coating supported on silicon or tantalum substrate anodes and stainless steel cathodes was reported.\textsuperscript{198} The process worked by volatilizing of liquid PCE, followed by the treatment. BDD on silicon substrate anode reached a PCE removal efficiency of 75.7% in 2 hours, while BDD on tantalum substrate achieved a PCE removal efficiency of 90.5% in 2 hours.\textsuperscript{198} Complete degradation of PCE was reported at pH 7 in 4 hours using nano-magnetite catalyzed with glutathione, with oxalic acid as the major by-product.\textsuperscript{199}

**Trichloroethene (TCE).** Degradation of TCE by sodium percarbonate activated with Fe(n)/citric acid complex in the presence of surfactant Tween-80 has been described. At optimal conditions, 93.2% degradation efficiency was achieved in 15 minutes.\textsuperscript{200} TCE was degraded using nanoscale calcium peroxide activated by Fe(n)/FeS, which enhanced generation of hydroxyl radicals, achieving 99.5% TCE removal efficiency in groundwater.\textsuperscript{201} Polyvinyl alcohol coated nano calcium peroxide activated by Fe(n)/FeS or Fe(n)/FeS has been used to degrade TCE, with maximum degradation of 91% and 95% for Fe(n)/FeS or Fe(n)/FeS activated polyvinyl alcohol coated nano calcium peroxide, respectively.\textsuperscript{202} Sequential anaerobic and aerobic treatment in the presence of the cyclic ether stabilizer 1,4-
dioxane degraded TCE. The anaerobic treatment used halorespiring consortium SDC-9 and effectively removed TCE, forming vinyl chloride (VC) and cis-dichloroethene (cis-DCE) as by-products. These by-products were removed along with the 1,4-dioxane during the subsequent aerobic bioaugmentation with Azotobacter sp. DD4.203

Other chlorinated organic water pollutants. Bimetallic zero-valent iron nanoparticles have been reported to degrade several chlorinated organic compounds, such as vinyl chloride (VC), 1,2-dichloroethene (DCE), TCE, and PCE. Bimetallic zero-valent iron nanoparticles with palladium and with nickel have completely degraded all compounds within 24 hours. VC, DCE, and TCE were completely degraded in 2 hours. PCE was degraded by about 97% and about 89% in 4 hours using Pd or Ni modified zero-valent iron nanoparticles, respectively, and complete degradation was achieved in 24 hours for both materials.204 Degradation of chlorinated volatile organic compounds from contaminated groundwater was achieved by an O3-bubble column reactor with a carrier-bound TiO2/ultraviolet light system, with degradation efficiencies of 98% for cis-1,2-DCE, TCE and PCE and of 85% for trichloromethane without detectable by-product formation.205 TCE and cis-1,2-DCE were degraded with Cupriavidus sp. CY-1 bacteria, whose growth was supplemented with TCE or cis-1,2-DCE and phenol or Tween 80 as co-substrates. Use of CY-1 bacteria, whose growth was augmented by phenol, TCE and cis-1,2-DCE were converted into poly-β-hydroxybutyrate (PHB), which is a biodegradable plastic.206

Recent progress in the destruction of brominated organic water pollutants

Tetrabromobisphenol-A (TBBPA). Peroxymonsulfate in aqueous solution was activated by Ce, Sn, or Sb doped copper ferrite, CuFe2O4, catalysts prepared by a sol–gel combustion method, to degrade TBBPA.207 A TBBPA removal efficiency of 90.1% in weakly basic conditions was achieved with Sn-doped CuFe2O4.207 In another study, dielectric barrier discharge was used to completely decompose TBBPA in wastewater in 12 minutes, forming phenol, bisphenol A, catechol, hydroquinone, and 3,5-dibromophenol as by-products.208 Bimetallic Co/Fe metal–organic frameworks/cellulose nanofiber membrane as a catalyst in a sulfate radical advanced oxidation process activated peroxymonsulfate and completely degraded TBBPA in 30 minutes at optimal conditions.209

2,4,6-Tribromophenol (TBP). An in situ peroxymonsulfate oxidation process with added chloride completely degraded TBP in salty wastewater, albeit with formation of undesired persistent halogenated products.210 Ultraviolet photolysis of TBP in the presence of hydroxylamine achieved a debrornination rate of 89.9% in 1 hour.211

Hexabromocyclododecane (HBCD). Near-complete aerobic biodegradation of aqueous HBCD was obtained by Rhodospseudomonas palustris VSC3 strain at 35 °C and neutral pH, forming bromide ions, pentabromocyclododecanol, and pentabromocyclododecane as by-products.212 Isotope-labeled [13C]HBCD was efficiently mineralized in 5 days into 13CO2 using organic montmorillonite-supported nanoscale zero-valent iron coupled with the bacterial strain Citrobacter sp. Y3.213 HBCD removal and mineralization was obtained by an ultrasound-based advanced oxidation process, which completely degraded HBCD and accomplished 72% of total organic carbon removal in 40 minutes.191 Complete degradation of HBCD was observed using nanoscale zero-valent aluminum in 8 hours in an ethanol/water solution at 25 °C, producing completely debrorninated cyclododecatriene with 67% yield.214 A ball-milled aluminum-carbon composite has been prepared to enhance the absorption and degradation of HBCD, completely absorbing HBCD in water in 1 hour and debrominating 63.44% of the pre-sorbed HBCD in 62 hours.215 We note that zero-valent first-row transition metals or aluminum may oxidize in ambient aqueous conditions that are needed for global scalability.

2,2',4,4'-Tetrabromodiphenyl ether (BDE-47). Reduction at zero valent zinc with cetyltrimethylammonium chloride surfactant achieved a BDE-47 removal efficiency of 98.6% in 1 hour, followed by a Fenton oxidation that decomposed all obtained debromination products into short-chain carboxylic acids that were mineralized in 2 hours.216 Complete degradation of BDE-47 was achieved in 3 hours with a thermally activated persulfate system, forming one low-toxicity oxidation product.217 A photocatalytic process using Ag/TiO2 was developed for the degradation of BDE-47 in Triton X-100 surfactant solution under anaerobic conditions, predominantly producing diphenyl ether and the harmful bromodiphenyl ethers BDE-28, BDE-15, BDE-3,218 which were found to be phytotoxic,219 or exhibited hepatic220 or reproductive toxicity221 in mice. BDE-47 was degraded using a Fe(II)-catalyzed peroxymonsulfate activation process with the addition of gallic acid to accelerate the cycling of Fe, which enhanced peroxymonsulfate activation, reaching a degradation efficiency of 85% in 72 hours.222 A functional bacterial consortium QY2 with an addition of methanol to enhance degradation efficiency and accelerate the debromination, hydroxylation, and phenyl ether bond breakage of BDE-47 completely removed BDE-47 in 7 days.223

Destructive remediation of fluorinated organic water pollutants including PFAS

The destructive remediation of fluorinated organic compounds, particularly PFAS, is an area of intense research. Methods for defluorination of the common PFAS chemical perfluorooctanoic acid (PFOA) have been reported by electrochemical reduction at a Rh/Ni cathode in dimethyl formamide via hydrodefluorination,224 hazardous γ-irradiation with a 60Co source in an alkaline solution under Na2-saturated conditions,159 and mineralization of perfluorocarboxylic acids, including PFOA, via the formation of rapidly decomposing carbanions in polar, aprotic dimethyl sulfoxide electrolyte; the carbanion-based mechanisms can only operate in water-free, polar, aprotic solvent and fail to degrade sulfonic acid PFAS, such as PFOS.225 Further, 19F-NMR was used to quantify PFOA defluorination, which appeared to have a detection threshold of ≥5 mM (approx. 2000 ppm PFOA).225 Globally scalable, viable technologies must work in aqueous media and
enable destruction of PFAS with much lower concentrations. Perfluorocarboxylic acids, such as perfluoro-butanolic, penta-
noic, hexanoic, heptanoic, and octanoic acid (PFOA), were
mineralized using a Ce-doped nanocrystalline PbO2 film elec-
trode,226 the toxicity of lead poses challenges. While these
reports are mechanistically intriguing, only cost- and energy-
saving aqueous methods that utilize nontoxic, nonprecious
materials and renewable electricity will be viable and sustain-
able on a global scale. Electrooxidation of PFOA and PFOS at
Magnéli-phase Ti4O7 ceramic anodes outperformed mineraliza-
tion at Ce-doped PbO2 and Ti-modified boron-doped diamond
electrodes, due to faster oxidation rate.227 PFOA in water was
degraded by ultraviolet-visible light assisted Zn2Cu1-xFe2O3-
xal acid system, using a ferrite-based catalyst that allowed for
magnetic catalyst recovery.228

Technoeconomic analyses of destruction techniques are
indispensable to assess viability on a global scale. Significant
research has been done to determine the most efficient destruct-
tion techniques.27 Energy efficiency is important to lower
operational costs and improve carbon footprints, whereas
capital expenditures matter for assessing the affordability of
units. Estimated energy and capital cost requirements of existing
PFAS destruction techniques, based on literature data,167,229–237 are shown in Fig. 4. Capital expenditure values refer to cost of equipment in the United States, are given in U.S.
dollars, and are needed to treat at least one cubic meter of
polluted water.

Incineration requires an initial investment of $41 938 050 for
a one-line “turn-key” incineration plant.83 The average amount of
energy required for incineration is 0.45 kW h m⁻³ in the U.S.,
which has been measured and varies depending on the country
and the type of incineration plant used.233 The reported initial
investment cost of γ-irradiation is $4 176 150, which includes
the sum of the cost of the electron beam accelerator with
lifespan of 15 years and personnel costs needed to run a γ-
irradiation facility.228 The equivalent electrical energy require-
tment to achieve 90% sulfadiazine degradation by γ-irradiation
from a 60Co source, taken here as a proxy for PFAS degradation,
at a constant dose rate of 6.69 kGy h⁻¹ has been reported to be
18 kW h m⁻³. The capital investment for non-thermal plasma231,237 of $92 329 was obtained from a capital cost
approximation for industrial wastewater plants.163,240 The
energy required to achieve a high removal rate of PFOA from
water using non-thermal plasma is 100 kW h m⁻³, which was
deduced from the energy efficiency of non-thermal plasma
setups.237 Sonolysis by ultrasonication has a capital investment
cost of $9 390 000, which has been calculated to include the part
replacement cost, labor cost, analytical costs, chemical costs,
and electrical costs.230 The energy requirement for sonolica-
tion (1475 kW h m⁻³) was calculated using the energy efficiency
of ultrasonication in g (kW h)⁻¹.235,241

Chemical oxidation of PFOA by stoichiometric amounts of
permanganate,242 hydrogen peroxide, or persulfate246 is cost-
prohibitive and creates large amounts of chemical waste.
Methods based on electrochemical processes have gained popu-
larit because of lower energy demands than physical destruction
methods, i.e. incineration, γ-irradiation, non-thermal plasma,
and sonolysis. PFAS destruction by supercritical water oxidation244
requires high initial investment;245 we were unable to find
numbers for investment costs. The thermal energy requirement
for an efficient supercritical water generation facility is 5 MW for
250 metric tons of water per day.246

Electrooxidations of PFAS at expensive, often toxic, specia-
lized anodes are nonviable.226,235,247–257 The inter-electrode
distance matters in electrolyzers because smaller distances
are concomitant with less ohmic losses.258 A generally accepted
upper limit for inter-electrode distance in aqueous systems is
10 cm, which necessitates 10 m² geometric electrode area to
treat 1 m³ of polluted water,258 rendering boron-doped dia-
mond (BDD) electrodes cost-prohibitive.259 At smaller inter-
electrode distances, which generally result in higher elec-
trocatalytic performance, the geometric electrode area require-
ment increases for treatment of a 1 m³ batch, making the
economics of BDD electrodes even more unfavorable. The
energy required to halve an initial PFOA concentration of
15 mg L⁻¹ with a BDD electrode of 38 cm² geometric area
and an inter-electrode distance of 4 mm was reported as
180 W h L⁻¹ at 50 mA cm⁻², for the treatment of 250 mL
solution.234 Conversion of these numbers to the treatment of
1 m³ of polluted water requires BDD electrodes of 15.2 m² at
a cost of $8.58 million229 and 180 kW h m⁻³ electrical energy
(Fig. 1). Electrochemical degradation of PFOA on ultra-
nanocrystalline BDD coated on niobium electrodes additionally
produced toxic perchlorate.234 Ultraviolet-light-assisted electro-
chemical PFAS defluorination required cost-prohibitive plat-
umine electrodes and N₂-saturated electrolyte.260 Ergo,
potentially viable PFAS destruction technologies must be more
cost-effective and energy-saving to achieve economic feasibility
and reduce carbon emissions.

Recent progress in the destruction of PFAS
Perfluorooctanoic acid (PFOA) has been degraded anaerobically
to shorter chain perfluoroalkyl carboxylic acids and produced
fluoride in biosolids using Acidimicrobium sp. strain A6 and ferrihydrite.  

PFOA has also been degraded efficiently by 80% over ball-milled boron nitride in deionized water or by 60% in simulated drinking water using photocatalysis for 2 hours.  

The photocatalytic degradation of PFOA under UV-A and UV-C illumination with boron nitride was improved by using a composite of boron nitride and titanium oxide instead of neat boron nitride or titanium oxide. However, complete mineralization was not achieved and only shorter chain perfluorinated carboxylic acids were produced. The composite was capable of degrading PFOA by 68% in 7 hours using natural sunlight.  

PFOA was degraded via a photocatalytic process that used a carbon-modified bismuth phosphate composite, absorbing PFOA in 2 hours and achieving nearly complete decomposition in situ in 4 hours under UV irradiation.  

Another composite that has been developed for the photocatalytic degradation of PFOA in water is iron (hydr)oxides/carbon sphere (FeO/CS) composite. This material almost completely adsorbed PFOA in 1 hour, which subsequently underwent photodegradation and defluorination. During this process, PFOA was photodegraded by 95.2% and defluorinated by 57.2% in 4 hours.  

Another photocatalytic process that used UV light and Bi_{2}O_{3}(PO_{4})_{2} in acidic conditions has been reported to degrade PFOA. However, this process was unable to degrade shorter chain PFAS unless some changes were made to the reactor system. With this system, challenges for implementation in real waters exist because the reaction was quenched by chloride and sulfate. Complete defluorination of PFOA was achieved after 6 hours in water using a dual-frequency ultrasonic activated persulfate. This method can be used for other PFAS compounds, but not as effectively.  

An electrochemical degradation process for PFOA using sodium sulfate has been developed, which enabled 99.5% degradation and 50% fluoride generation after 4 hours. A sorptive photocatalyst Fe/TNTs@AC, which was based on activated carbon and titanium oxide, was synthesized and used for PFOA degradation. This catalyst completely absorbed PFOA in 1 hour, degraded it by 90% in 4 hours using UV radiation, and then mineralized 62% of the degraded PFOA to fluoride. Another photocatalytic process that has been developed to degrade PFOA in aqueous solutions used In_{2}O_{3} nanoparticles. This process worked most efficiently in acidic (pH = 2) conditions and successfully decomposed most of PFOA to fluoride and carbon dioxide within 90 minutes under UV irradiation, while also achieving 95.99% of PFOA defluorination.  

Chemical mineralization of perfluorocarboxylic acids is mechanistically intriguing, but works only in polar, non-protic electrolytes, such as dimethyl sulfoxide (DMSO), hampering global scalability, and fails to degrade sulfonic acid PFAS, such as PFOS.  

Perfluorooctane sulfonic acid (PFOS) degradation has been reported, using sonolysis by 96.9%, 93.8%, and 91.2% at 400 kHz, 500 kHz, and 1000 kHz, respectively, in 4 hours. Another method to degrade PFOS in an aqueous solution used reverse vortex flow gliding arc plasma; PFOS was degraded by 93.1% in 1 hour. This method can also be used to degrade other PFAS compounds, such as PFOA or PFDA and others.  

Both PFOA and PFOS were defluorinated by 88% in 1 hour and 92% in 24 hours, respectively, using a UV light in a system that contained sulfite and iodide. Adding iodide to the UV light illuminated sulfite system greatly accelerated the defluorination of many PFAS. This system has achieved a complete removal of both PFOA and PFOS from concentrated mixtures in NaCl brine. Electrooxidation using titanium suboxide anodes were used to degrade multiple PFAS compounds, such as PFOA and PFOS, whose concentrations decreased very quickly and approached zero in 1 hour. Another method to degrade PFOA and PFOS as well as other PFAS compounds is γ-irradiation, using a 60Co source. PFOS degradation was more efficient with branched PFOS isomers compared to linear molecules. Branched PFOS isomers were degraded almost completely, while PFOA was degraded by 87%. A non-thermal plasma generator was custom-built to remove PFOA, perfluorohexanoic acid (PFHxA), and PFOS from water in both ultrapure and groundwater. In 30 minutes, PFOS was degraded completely in ultrapure water and by 85% in groundwater. PFHxA was degraded by 35% in ultrapure water and by 40% in groundwater, while PFOA degradation reached about 50% in both water systems. PFOS and PFOA were significantly degraded in soil and groundwater by high dose electron beam technology. This process enabled the decrease of PFOS and PFOA concentrations in groundwater by 87.9% and 53.7%, respectively. A duo-functional tri-metallic-oxide hybrid photocatalyst has been developed for the degradation of many PFAS compounds. It possessed a high adsorption capacity and achieved 99.8% and 99.4% adsorption efficiency for PFOS and PFOA respectively, and it exhibited a high defluorination rate up to 67.6% for PFOS and 74.8% for PFOA. With this catalyst, PFOS was degraded by 95.5% in 5 hours, while PFOA was degraded by 98.9% in 30 minutes. Boron-doped graphene sponge anodes have been reported for the degradation of PFAS compounds by electrochemical oxidation. This method had a higher removal efficiency for longer-chain than for short-chain PFAS, but its defluorination efficiency was lower than that of other methods. GenX, which is a short-chain PFAS, was mineralized by an electro-Fenton process that paired a graphene-coated nickel foam electrode with a boron doped diamond electrode. This process achieved 92.2% mineralization after 6 hours of treatment.  

Aqueous advanced redox processes  

Advanced oxidation processes, advanced reduction processes, and combined hybrid processes have emerged as promising strategies in water remediation due to potentially high organohalogen destruction efficiencies. These processes can have rapid reaction rates, destroy pollutants without generating solid waste, do not require chemical oxidants, high pressures, or high temperatures, and can be powered by sustainable renewable electricity. The advantages of advanced redox processes have led to intense research, such as photolytic, photochemical, photocatalytic, cavitation, electrochemical, and ionizing radiation approaches for water remediation, as well as combinations of these methods.
Advanced oxidation processes (AOPs) generate and utilize highly reactive species with high oxidation potentials that are capable of cleaving carbon–halogen bonds of pollutants in wastewaters.\textsuperscript{306} Oxidants are often radicals under aerobic conditions, such as the hydroxyl radical (\(\cdot\)OH, aqueous lifetime 0.02 \(\mu\)s), superoxide radical anion (\(\cdot\)O\(_2^–\)), aqueous lifetime 1.3 \(\mu\)s), sulfate radical anion (\(\cdot\)SO\(_4^–\)), aqueous lifetime 30–40 \(\mu\)s), and sulfite radical anion (\(\cdot\)SO\(_3^–\)), in addition to potent non-radical species, such as hydrogen peroxide (H\(_2\)O\(_2\)) and singlet oxygen (O\(_2^\cdot\), aqueous lifetime 3.5 \(\mu\)s).\textsuperscript{305,306–308}

Advanced reduction processes (ARPs) produce highly reactive species with high reduction potentials to cleave carbon–halogen bonds of aqueous pollutants.\textsuperscript{302} Reductants generated by ARPs require completely anaerobic conditions and are comprised of radicals, such as the sulfur dioxide radical anion (SO\(_4^–\)) and hydrogen radical (H\(^*\)), as well as non-radical hydrated electrons (e\(_{\text{aq}}^*\) aqueous lifetime 0.43 or 8.6 \(\mu\)s at pH 7.0 or 9.5, respectively).\textsuperscript{113,287,304}

Oxygen-free conditions are often impractical, especially since the water oxidation half reaction can produce O\(_2^\cdot\),\textsuperscript{305,306} membranes that separate oxidation and reduction half reactions cannot completely exclude oxygen crossover,\textsuperscript{307} and airtight seals are inherently challenging on a large scale.

**Mechanistic aspects of electrocatalytic aqueous advanced redox processes**

A quantitative mechanistic understanding of aqueous advanced redox processes is lacking to date, albeit urgently needed to accelerate the development of viable aqueous electrocatalytic organohalogen destruction techniques. Radicals and reactive oxygen species play a major role in aqueous advanced redox processes, and the mechanisms of their formation and reactions with organohalogen must be understood in detail. Electrocatalysts significantly lower energy requirements for electrochemical transformations,\textsuperscript{305} especially in aqueous systems, where potential-leveling by proton-coupled electron transfer (PCET) decreases needed energy inputs.\textsuperscript{308}

**Reactive oxygen species of the water–oxygen system**

Aerobic aqueous processes that produce H\(_2\)O\(_2\), \(\cdot\)OH, HOO\(^*\), or OO\(^*\) are based on the electrochemical transformations of the water–oxygen system (Fig. 5). Most of the transformations are electrochemical oxidations or reductions that proceed through energy-saving, potential-leveling PCET steps, which require that equal numbers of protons and electrons are transferred.\textsuperscript{308}

Reactive oxygen species that are relevant for organohalogen destruction, i.e. H\(_2\)O\(_2\), \(\cdot\)OH, HOO\(^*\), and OO\(^*\), can be produced directly or via H\(_2\)O\(_2\) decomposition. Water oxidation can only produce O\(_2\), H\(_2\)O\(_2\), or \(\cdot\)OH through direct electrocatalysis. The one-electron-one-proton or two-electron-two-proton water oxidation reactions, given here together with standard potentials \(E^0\) in V vs. the standard reference electrode (SHE), i.e. H\(_2\)O \(\rightarrow\) O\(_2\)\(_{\text{aq}}\) + 4H\(^+\) + 4e\(^–\), \(E^0 = 2.38\) V\(_{\text{SHE}}\), or 2H\(_2\)O \(\rightarrow\) H\(_2\)O\(_2\) + 2H\(^+\) + 2e\(^–\), \(E^0 = 1.76\) V\(_{\text{SHE}}\), are kinetically easier than the four-electron-four-proton reaction, i.e. 2H\(_2\)O \(\rightarrow\) O\(_2\) + 4H\(^+\) + 4e\(^–\), \(E^0 = 1.23\) V\(_{\text{SHE}}\), but thermodynamically more uphill.\textsuperscript{3} Molecular oxygen can be reduced to H\(_2\)O\(_2\), \(\cdot\)OH, HOO\(^*\), or OO\(^*\) (Fig. 5).\textsuperscript{309} Electrochemical reductions and oxidations that involve the transfer of less electrons and protons are kinetically faster than those that require the movement of more electrons and protons in the H\(_2\)O–O\(_2\) system (Fig. 5). The electronic and chemical structures of intermediates of one-electron-one-proton transformations are known from computational density functional theory work, which cannot accurately capture concerted two-electron steps.\textsuperscript{2,3,6} Together with the thermodynamic potentials below, these kinetic considerations allow as a function of electrolyte pH estimates which reactant species are likely formed in the highest concentrations for efficient destruction of halogenated organic water pollutants.

Hydrogen peroxide is a precursor for \(\cdot\)OH, HOO\(^*\), or OO\(^*\)-radical generation (Fig. 5) and, therefore, often called a pre- or pro-radical species. Hydrogen peroxide is a strong oxidant but reacts slowly with organics, so that it is often activated by alkali, activated carbon, heat, ultraviolet light, or transition metals,\textsuperscript{296} such as iron-containing catalysts, which can in the presence of H\(_2\)O\(_2\) serve as initiators for propagation reactions that generate \(\cdot\)OH, HOO\(^*\), OO\(^*\), and HOO\(_2^*\) species \(\text{via Fenton, Haber–Weiss, or photo-Fenton reactions.}^{310–311}\) Addition of H\(_2\)O\(_2\) to the electrolyte was found to quench the production of toxic perchlorate at BDD electrodes.\textsuperscript{314}

**Thermodynamic potentials of reactive oxygen species**

The thermodynamic potentials of reactive oxygen species determine their oxidation or reduction strengths in AOPs and ARPs of halogenated organic water pollutants. The protonation state and thermodynamic potential of aqueous reactive oxygen species depend critically on the electrolyte pH (Table 3). For example, at pH 0, \(\cdot\)OH and HOO\(^*\) are strong aqueous oxidants with standard potentials (i.e. thermodynamic potentials at pH 0) of 2.73 and 1.66, respectively, and both radicals possess sufficient thermodynamic driving force for PFAS oxidation. In contrast, at pH 14, the deprotonated hydroxyl radical anion (O\(^*\)) possesses a thermodynamic potential of 1.77 V, whereas the thermodynamic potential of the superoxide radical anion (O\(_2^*\)) is only 0.65 V, which is insufficient to oxidize PFAS.

The protonation state of chemical species depends on their pK\(_a\) value and the pH of the aqueous solution; if the pH value is
Mechanistic role of oxygen radicals for PFAS destruction

Reactive oxygen radicals, such as \( \text{OH}, \text{O}^\cdot, \text{HO}_2^\cdot, \text{OO}^\cdot \), are key species in AOPs and ARPs for C-C and C-F bond cleavage. Superoxide radical anions (\( \text{OO}^\cdot \)) can oxidize PFAS molecules; \( \text{OO}^\cdot \) can also act as a reductant and is the predominant species at pH > 5, as \( \text{HOO}^\cdot \) has an aqueous \( pK_a \) of 4.8.\(^{309}\) Hydroxyl radicals in aqueous solution are widely considered insufficient for PFOA or PFOS degradation,\(^{310,323,324}\) because \( \text{OH}^\cdot \) radicals have an approximately 10\( \times \) shorter aqueous diffusion distance than \( \text{OO}^\cdot \) radicals.\(^{325,326}\) Quenching experiments with saturated alcohols that selectively scavenged \( \text{OH}^\cdot \) radicals had no effect on the degradation of PFAS.\(^{327,328}\) The exact role of \( \text{O(H)} \) radicals in aqueous electrocatalytic PFAS destruction is still debated. Recently, decreased degradation efficiency was observed in the presence of unsaturated allyl alcohol that is capable of quenching \( \text{OH}^\cdot \) radicals in the vicinity of the anode, suggesting that adsorbed \( \text{OH}^\cdot \) radicals played a significant role in PFAS degradation.\(^{328,329}\) Adsorbed \( \text{OH}^\cdot \) radicals are physisorbed; analog surface-bound species are non-radical hydroxide anions (\( \text{OH}^- \)) that lack the thermodynamic driving force for PFAS destruction.\(^{309}\)

Auxiliary radicals and non-radical species

Addition of suitable solutes to aqueous media enables the formation of auxiliary radicals and non-radical redox agents in aqueous AOPs and ARPs. Reactive sulfur radicals are generated through dissociative reactions of persulfate, peroxomonosulfate, sulfate, or bisulfite to produce sulfate radicals, which are capable of assisting PFAS breakdown,\(^{26,243,301,304}\) whereas the dissociation of bisulfite or sulfate anions produces sulfite radicals and hydrated electrons in strictly oxygen-free conditions.\(^{113,304,330–332}\) Addition of iodide, dithionite, or ferro-cyanide to anaerobic electrolytes can aid the detachment mechanism to produce hydrated electrons.\(^{260,333}\) Dissociation of dithionite will produce reductive sulfur dioxide radicals.\(^{302}\) Sulfite assists PFAS degradation through formation of persulfite.\(^{323,334}\) Stoichiometric PFOA oxidation by permanganate has been observed.\(^{322}\) Borate is known to react with \( \text{H}_2\text{O}_2 \) to produce peroxoborates that are stable at pH 8 to 12 and highly reactive towards nucleophiles.\(^{335}\) Standard potentials of PFAS-relevant auxiliary species in aqueous solution are in Table S\(^{285,288–299}\)

Mechanistically, the initial attack on the pollutant occurs by radical addition to a carbon–carbon double bond or by the abstraction of a carbon-bound hydrogen after the generation of auxiliary radicals and species.\(^{336–338}\) In the case of perfluorocompounds, such as PFOA and PFOS, that do not contain carbon-bound hydrogens and C–C double bonds, a different initial oxidation step is required that starts with the elimination of the head group in photo- or electrochemical processes.\(^{282,339,340}\) An electron transfer from the carboxylic acid to the anode creates a carboxyl radical that undergoes decarboxylation to produce the carbon-centered perfluoroalkyl radical (\( \text{C}_n\text{F}_{2n+1}^\cdot \)) and \( \text{CO}_2. \)\(^{176,183,274}\) Likewise, perfluorinated sulfonic acids are desulfonated via an analogue initial electron transfer.\(^{258,282,341,342}\) The generated carbon-centered radicals quickly react with surrounding dissolved oxygen, water, or other radicals to form smaller carbonyl species. Once initiated, subsequent propagation reactions between the parent and

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### Table 3

<table>
<thead>
<tr>
<th>Reduction reaction at pH 0</th>
<th>( E ) [V] at pH 0</th>
<th>Reduction reaction at pH 7</th>
<th>( E ) [V] at pH 7</th>
<th>Reduction reaction at pH 14</th>
<th>( E ) [V] at pH 14</th>
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<tr>
<td>( \text{O}_2 \rightarrow \text{HOO}^\cdot )</td>
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<td>( \text{O}_2 \rightarrow \text{H}_2\text{O}_2 )</td>
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<td>( \text{O}_2 \rightarrow (\text{H}_2\text{O} + \cdot \text{OH}) )</td>
<td>+0.73</td>
<td>( \text{O}_2 \rightarrow (\text{H}_2\text{O} + \cdot \text{OH}) )</td>
<td>+0.31</td>
<td>( \text{O}_2 \rightarrow (\text{OH}^- + \cdot \text{O})^\cdot )</td>
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<td>( \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \cdot \text{OH} )</td>
<td>+1.229</td>
<td>( \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \cdot \text{OH} )</td>
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<td>( \text{O}_2 \rightarrow \text{H}_2\text{O} + \cdot \text{OH} )</td>
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<td>( \text{OO}^\cdot \rightarrow \text{H}_2\text{O}_2 )</td>
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<td>( \text{H}_2\text{O} \rightarrow \text{H}_2\text{O} )</td>
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### Table 4

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<th>Ref.</th>
<th>( pK_a )</th>
<th>Ref.</th>
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<td>( \cdot \text{OH} )</td>
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<td>319</td>
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<td>309</td>
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<td>( \text{PFOS} )</td>
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<td>321</td>
<td>( \cdot \text{C}_2\text{F}_5\text{OH} )</td>
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</table>

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### Table 5

<table>
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<tr>
<th>Reaction</th>
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<tr>
<td>( \text{SO}_4^{2-} \rightarrow \text{SO}_2^{2-} )</td>
<td>2.44</td>
</tr>
<tr>
<td>( \text{SO}_4^{2-} \rightarrow \text{SO}_3^{2-} )</td>
<td>0.73</td>
</tr>
<tr>
<td>( \text{SO}_3^{2-} \rightarrow \text{SO}_2^{2-} + \text{SO}_4^{2-} )</td>
<td>1.44</td>
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<td>( \text{SO}_2^{2-} \rightarrow \text{SO}_3^{2-} )</td>
<td>0.81</td>
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<td>( \text{H}_2\text{BO}_3^- + 5\text{H}_2\text{O} \rightarrow \text{B}_4\text{H}_4^- + 8\text{OH}^- )</td>
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<tr>
<td>( \text{MnO}_4^- \rightarrow \text{MnO}_2 )</td>
<td>1.70</td>
</tr>
<tr>
<td>( \text{e}^- \rightarrow \text{aq}^- )</td>
<td>-2.88</td>
</tr>
<tr>
<td>( \text{H}^+ \rightarrow \text{H}^\cdot )</td>
<td>-2.31</td>
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</table>
daughter species of the decomposing pollutant with highly reactive, strong oxidants will ultimately lead to complete mineralization of perfluorinated compounds.286

Reductive dehalogenation via hydrated electrons that are generated by ultraviolet photolysis from sulfite requires oxygen-free conditions, which are impractical on a large scale. Added sulfite can effectively deoxygenate aqueous solutions, forming sulfate, which in turn can form SO₄⁻ for AOPs. Sulfite promotes the formation of SO₂⁻, which is a mild oxidant341 that reacts rapidly with oxygen to produce SO₃⁻ and subsequently SO₄⁻ and •OH radicals, which are stronger oxidants and can more effectively degrade organohalogen pollutants.301

Electrocatalytic aqueous generation mechanisms of reactive species

Electrocatalytic AOP and ARP mechanisms proceed through direct electrocatalysis at materials surfaces,96,115,283,344 indirect solution reactions,176,345 or assisted reactions at materials and in solution.332,346,347 In aqueous electrolyte without auxiliary solutes, aerobic electrocatalysis encompasses anodic water oxidation to H₂O₂ (precursor for AOPs), •OH radicals (for AOPs), or O₂ (loss process),3 and cathodic oxygen reduction at suitable catalysts348,349 to H₂O₂, •OH or OO• radicals, or water; H₂O₂ reduction to water can also occur (see Fig. 5 and 6A). Produced reactive species can diffuse into the bulk solution if they are sufficiently long-lived (see aqueous advanced redox processes) and react in indirect reactions to produce additional reactive species. The aqueous lifetime of •OH is 0.02 μs, whereas that of OO• is 1.3 μs, resulting in a diffusion distance of OO• radicals (30 nm) that is approximately 10× longer than that of •OH radicals (4.5 nm).325,326 The diffusion distances of both •OH and OO• radicals are too short for diffusion from electrodes into the bulk solution, but solution •OH and OO• radicals can be created by decomposition of H₂O₂ in strongly acidic or alkaline water.350 In the absence of dioxygen, i.e. in anaerobic media, anodic water oxidation produces •OH radicals, H₂O₂, or O₂, which requires deoxygenation of the aqueous electrolyte, e.g. by sulfite,341 to ensure completely oxygen-free conditions. Direct, unassisted cathodic electrocatalysis in anaerobic electrolyte consists of H₂O₂ reduction to water (Fig. 6B). Deep-ultraviolet light,352 radiolysis,297 or sonolysis297 enable assisted electrocatalytic production of reactive oxygen radicals and, in O₂-free aqueous environment, hydrated electrons, e⁻aq, and hydrogen radicals, H⁺. Assisted aerobic electrocatalysis creates •OH radicals, H₂O₂, or O₂ anodically by water oxidation, and H₂O₂, •OH, or OO• by

Fig. 6 Generation of radicals and reactive species in aqueous electrocatalysis for use in advanced redox processes; ref. el., reference electrode. Species produced at electrodes are in white, species produced in bulk solution are in blue in the blue circles; the yellow stars indicate assisting processes, such as deep ultraviolet light irradiation, radiolysis, or sonolysis. Anodic dioxygen (O₂) may be formed, depending on the water oxidation catalyst. Species in braces are short-lived intermediates. (A) Electro catalysis in aerobic electrolyte, (B) electrocatalysis in anaerobic electrolyte, (C) assisted electrocatalysis in aerobic electrolyte, (D) assisted electrocatalysis in anaerobic electrolyte; e⁻aq, hydrated electron.
cathodic oxygen reduction; produced H₂O₂ immediately decomposes to *OH radicals by deep-ultraviolet light,³⁵² or *OH or OO⁻ radicals by radiolysis²⁹⁷ or sonolysis²⁹⁷ processes that assist electrocatalysis (Fig. 6C). Assisted anaerobic electrocatalysis produces *OH radicals, H₂O₂, or O₂ by anodic water oxidation (Fig. 6D). Elimination of O₂ to ensure anaerobic conditions and immediate decomposition of H₂O₂ to *OH radicals by deep-ultraviolet light,³⁵² or *OH or OO⁻ radicals by radiolysis²⁹⁷ or sonolysis²⁹⁷ leave only *OH radicals (or OO⁻ radicals if radiolysis or sonolysis were used) as reducible species for the cathode half reaction (Fig. 6D); the highly energetic assisting processes continuously generate *OH (or OO⁻) radicals in the entire electrochemical cell, including in the vicinity of the cathode. Assisted anaerobic electrocatalysis (Fig. 6D) additionally enables the production of hydrated electrons, e⁻ₐq, and hydrogen radicals, H⁺, which are needed for ARPs, and which are only accessible in completely O₂-free aqueous electrolyte.

The aqueous generation mechanisms of reactive oxygen species and radicals are highly entangled, creating complex reaction networks. Much research has been dedicated to the elucidation of mechanisms. Pollutant degradation via AOPs and ARPs involves three principal steps: (i) reactive species generation, (ii) initial attack on the pollutant, and (iii) subsequent attacks on the pollutant until mineralization is complete.¹¹³ Direct reactions occur at the electrode surface through electron transfers between the electrode and the chemical substrate.²⁸³ In electrochemical oxidation reactions, the anodically generated holes must have sufficient electrochemical potential to create oxidizing agents, without turning on the four-electron-four-proton water oxidation electrocatalysis to dioxygen. Suppression of O₂ evolution requires applied potentials at or below the oxygen evolution potential, which is comprised of the thermodynamic potential and kinetic overpotential at the chosen pH conditions and catalyst materials.⁹⁶,¹⁰⁵,¹⁰⁶ Direct oxidation reactions are often slow because substrate adsorption at the anode controls the reaction rate. Due to these slow kinetics and limited useful applied anodic potential, direct electrocatalytic reactions typically do not result in complete mineralization of pollutants.⁹⁶

Quasi-direct redox reactions occur at the electrode–electrolyte interface via physisorbed or chemisorbed redox species,¹¹³,⁴⁴⁴ which are typically generated through reactions between the electrode and the aqueous electrolyte. Thus, the oxidizing strength in these processes is governed by the thermodynamic potential of the produced reactive species. Quasi-direct reactions have inherent mass transport limitations to and from the bulk solution because these processes must take place in the vicinity of the electrode–electrolyte interface.

Indirect processes occur in the bulk electrolyte, to where mediators migrate after electrochemical generation at the electrode–electrolyte interface, to react with pollutant species.¹⁷⁶,⁴⁴⁵ Reactive species for indirect AOPs and ARPs are typically long-lived to enable long diffusion distances into the bulk solution. Therefore, reactive oxygen species generated at the electrode–aqueous electrolyte interface are of limited use in these reactions due to their proclivity for recombination and short lifetimes despite being among the strongest oxidizing agents.³⁵³ Some halogenated redox agents have longer lifetimes in comparison to those of reactive oxygen species, however, their selective reactivity and lower oxidation strength limits their reaction efficiency in the bulk electrolyte. Other advanced redox species, like sulfate radicals, possess longer lifetimes and simultaneously similar or greater oxidation strengths compared to reactive oxygen species, enabling indirect redox reactions.¹⁶⁵,³³⁴,³³⁵

Indirect processes have been coupled with other advanced redox activation processes to further increase the degradation efficiency of electrochemical systems.³³²,³⁴⁶,³⁴⁷,³⁵⁶ Ultraviolet or visible light irradiation of electrochemical systems has most often been used. These coupled processes maintain similar reaction networks as dark electrochemical systems, with photo-activation of electrochemically generated mediators, so that increased concentrations of redox agents are produced at the electrode surface and within the bulk electrolyte.³³²,³⁴⁶,³⁴⁷

Photochemistry is frequently used to destroy pollutants and can be classified as three processes: photolysis, photochemical, and photocatalysis. Photo-assisted AOPs and ARPs have similar advantages as electrochemical processes, such as operation at ambient temperature and pressure, low operating costs, and no generation of waste streams.

Photolysis is the direct absorption of light by chemical substrates for direct degradation via homolytic bond scission or direct light absorption by water to produce highly reactive redox agents for indirect degradation.¹¹³ The mechanism of photolysis consists of three steps: (i) light absorption that excites electrons in the molecule, (ii) primary photochemical processes that transform photoexcited molecules or result in relaxation back to the ground state, and (iii) secondary thermal reactions that transform the intermediates that were produced in step (ii).³⁵⁷ Photolysis is limited to pollutants that exhibit large molar absorption cross sections and quantum yields, which restricts the overall applicability of photolysis.³⁵⁸ Previous research has demonstrated applications of photolysis for pollutant degradation,³⁵⁹–³⁶¹ but photolysis is mainly used for the inactivation of pathogenic microorganisms.³⁶²,³⁶₃

Direct ultraviolet photolysis of anaerobic water to form *OH radicals, H⁺ atoms, and hydrated electrons, e⁻ₐq (see Tables 3 and 5 for thermodynamic potentials) has been demonstrated with vacuum ultraviolet (VUV) wavelengths <200 nm, albeit with low quantum yields and very slow breakdown of PFAS.³⁶⁴,³⁶⁵ Use of VUV irradiation is impractical because of the high absorption cross section of most materials at wavelengths below 200 nm. Deep ultraviolet irradiation at 254 nm is inefficient for direct photolysis of PFOA.³⁶⁶ But deep ultraviolet light is capable of enhancing PFAS decomposition by AOPs of auxiliary chemicals (H₂O₂, SO₄²⁻, SO₃²⁻) via radical generation and indirect pollutant oxidation.³₂₃,³₂₄,³⁶⁷

Addition of transient chemical oxidants to water can overcome photolysis challenges and enhance the overall degradation efficiency of persistent pollutants³⁵⁵,³⁶⁸ in a process known as photochemical degradation. Mechanistically, photochemical
Highlight

The general mechanism of photocatalysis starts with adsorption of light with a photon energy equal to or greater than the bandgap of the semiconductor to photoexcite an electron in the photocatalyst material from the valence band to the conduction band, leaving a hole in the valence band. This photogenerated hole initiates oxidation reactions with the surrounding electrolyte to release reactive redox agents into the solution. Continually regenerated photo-holes and reactive species result in the oxidative destruction of pollutants.

Advanced redox processes for chlorinated and brominated organic compounds

Brominated and chlorinated pollutants are often degraded cathodically via ARPs because oxidation of liberated bromide or chloride produces toxic liquid bromine or chlorine gas, respectively. Nevertheless, Fenton-based AOPs have extensively been studied for the degradation of brominated and chlorinated pollutants. Fenton-based technology utilizes the reaction of ferrous ions with hydrogen peroxide, at an optimum pH, to generate hydroxyl radicals that react with pollutants in solution. While Fenton-based methods are popular due to their wide application range, cost effectiveness of iron, strong anti-interference ability, simple operation, and rapid degradation, significant disadvantages exist, such as the narrow working pH range and the generation of significant amounts of iron sludge. Brominated flame retardants were completely mineralized, whereas chlorinated trichloroethylene was not completely degraded. Fenton methods in pyrite suspension have been developed to enhance reaction kinetics of $\text{H}_2\text{O}_2$ decomposition to $\cdot\text{OH}$ radicals for more efficient pollutant degradation. Iron ions activated persulfate anions to produce sulfate radicals in a Fenton-like reaction for the chemical degradation of trichloroethylene. Photoelectrochemical systems have demonstrated enhanced AOP performance, synergistically degrading halogenated pollutants. Specifically, a photoelectrochemical system has been developed to degrade a series of chlorinated organic molecules to carbon dioxide, carbon monoxide, and chloride ions. Pulsed potential electrolysis has been shown to significantly increase mineralization efficiencies compared to constant...
potential electrolysis for chlorinated organic pollutants.\textsuperscript{395} In a gas diffusion device, 4-chlorophenol and 4-bromophenol were electrochemically dehalogenated to phenol.\textsuperscript{173}

Pairing Fenton processes with ultraviolet irradiation capitalizes on parallel reactive oxygen generation pathways. An ultraviolet-Fenton system achieved complete degradation of tetrabromobisphenol-A.\textsuperscript{396} Hybrid Fenton-like processes have been paired with other AOPs and ARPs, such as sonolysis by ultrasound.\textsuperscript{397,398} Hybrid systems have garnered much attention recently because of enhanced overall degradation rates. Sonophotocatalysis utilizes ultrasonic radiation and photocatalysis to synergistically generate more \( ^* \text{OH} \) radicals than either individual method by itself does, evidenced by the degradation of 2-chlorophenol.\textsuperscript{399} Hybrid systems that utilized ozone and \( \text{H}_2\text{O}_2 \) in a tube reactor nearly completely mineralized trichloroethylene and perchloroethylene in aqueous solution.\textsuperscript{400}

Advanced redox processes for fluorinated organic compounds including PFAS

Conventional wastewater treatment processes are inefficient for PFAS destruction because of the exceptional stability of C–F bonds (see Table 1 and Fig. 3).\textsuperscript{400} PFAS can be destroyed by AOPs and ARPs, particularly when aided by photo-assisted processes.\textsuperscript{400} Direct photolysis is ineffective for treating many PFAS chemicals because the optical absorption of most PFAS molecules is limited to the UV-C region (<220 nm); UV-C irradiation requires specialized equipment and skin-cancer safety precautions; system lifetimes were inherently lower than those of systems irradiated with longer wavelengths, adding to overall capital investments.\textsuperscript{390} Photocatalysis enhanced PFAS degradation, as was reported for 254 nm (deep ultraviolet) illumination of the benchmark photocatalyst \( \text{TiO}_2 \) for PFOA decomposition; irradiation with 315–400 nm light significantly decreased degradation performance, suggesting that the ability of the photocatalyst to generate sufficiently strong oxidants, such as \( ^* \text{OH} \) or \( \text{OO}^* \), controlled defluorination efficiency.\textsuperscript{401} Addition of persulfate to aqueous systems increased PFAS defluorination from negligible to nearly complete mineralization, via direct photocatalysis of persulfate to sulfate radicals.\textsuperscript{402–404} Photo-assisted electrochemical processes demonstrated enhanced degradation efficiencies of fluorinated compounds compared to dark electrochemical processes.\textsuperscript{260,341,405,406} The photo-Fenton process was utilized to increase transient radical concentrations compared to those generated by the dark Fenton process\textsuperscript{407} and concomitantly enhanced PFAS degradation.\textsuperscript{408} Addition of auxiliary chemicals to the electrochemical system benefitted the overall degradation efficiency of PFAS chemicals.\textsuperscript{280,330} Direct electrochemical and indirect hybrid electrochemical systems have been investigated for fluorinated pollutant degradation.\textsuperscript{234,260,280,339,341,405,406,409,410} Reported direct electrochemical PFAS degradation processes were most efficient when they occurred on boron-doped diamond (BDD) electrodes,\textsuperscript{234,339,409,410} which are cost-prohibitive on a large scale (see Fig. 4).

Mechanisms of electrochemical aqueous PFAS destruction

All PFAS electrooxidation pathways start with a direct electron transfer to the anode, which is rate-limiting according to density functional theory calculations,\textsuperscript{412} followed by decarboxylation (perfluorinated carboxylic acids, such as PFOA)\textsuperscript{176,183,274} or desulfonation (perfluorinated sulfonic acids, such as PFOS)\textsuperscript{415,282,341,342} to form a \( \text{CF}_2 \text{F}_{2n+1} \) radical, from which CF\(_2\) moieties are unzipped by \( ^* \text{OH} \) or \( \text{OO}^* \) radicals to form shorter-chain perfluoralkyl radicals, ultimately producing CO\(_2\) and HF, which can safely be mineralized as calcium-containing solids.\textsuperscript{411} Several reaction pathways have been proposed, depending on the chemical nature of the oxidant (Fig. 7).\textsuperscript{304,310,412} All reported mechanisms of aqueous electrochemical degradation of PFOA start with electron transfer to the anode and decarboxylation, liberating CO\(_2\), to form the \( \text{CF}_2 \text{F}_3 \) radical, which then further reacts with \( ^* \text{OH} \) to form \( \text{CF}_2 \text{F}_3 \text{OH} \) in the hydroxyl radical mechanism or with oxygen and protons in the hydrogen peroxide mechanism.\textsuperscript{304,310,412} Other auxiliary anions in aqueous solution, such as sulfate or borate, enhance the generation of superoxide radical anions or hydroxyl radicals, opening pathways that proceed through the hydrogen peroxide mechanism or hydroxyl radical mechanism, respectively (Fig. 7A). The intermediate \( \text{CF}_2 \text{F}_3 \text{OH} \) (structurally equal to \( \text{CF}_2 \text{F}_3 \text{OF}^{-} \)) is unstable and undergoes intramolecular rearrangement and hydrolysis, by which \( \text{CF}_2 \text{F}_3 \text{COO}^{-} \) is produced, effectively unzipping one \( \text{CF}_2 \) moiety as one CO\(_2\) and two HF molecules from the original \( \text{CF}_2 \text{F}_3 \text{COO}^{-} \) reactant.\textsuperscript{404} Alternatively, the \( \text{CF}_2 \text{F}_3 \) radical can react with dioxygen in the oxygen mechanism (Fig. 7A) to form the \( \text{CF}_2 \text{F}_3 \text{OO}^{-} \) radical, followed by decomposition of \( \text{CF}_2 \text{F}_2 \text{O}^{-} \) to perfluoroallyl radical and carbonyl fluoride.\textsuperscript{412}

Reported aqueous electrochemical degradation of PFOS starts with a direct electron transfer to the anode. Because the bond dissociation energy of the C–S bond (272 kJ mol\(^{-1}\)) in PFOS is lower than that of the C–C bonds (346 kJ mol\(^{-1}\)),\textsuperscript{413,414} or that of the C–F bonds (464.5–481.5 kJ mol\(^{-1}\)),\textsuperscript{415} desulfonation occurs after the initial electron transfer (mechanisms I and III).\textsuperscript{412–414} Nevertheless, mechanism II has been proposed, which unzips CF\(_2\) moieties before desulfonation.\textsuperscript{412} Desulfonation can follow different mechanistic pathways (Fig. 7B). In mechanism I, the initial electron transfer to the anode is followed by the formation of a very unstable \( \text{CF}_2 \text{F}_4 \text{SO}_3^{-} \) radical that reacts with water to form \( \text{CF}_2 \text{F}_7 \), which undergoes hydroxylolation and hydrolysis reactions to form deprotonated PFOA and HF. This cycle repeats seven times to produce CO\(_2\) and HF.\textsuperscript{413,414} In the presence of hydrogen radicals (\( \text{H}^* \)), aqueous electrocatalytic PFOS degradation follows mechanisms II or III, where PFOS (\( \text{CF}_2 \text{F}_3 \text{SO}_3^{-} \)) reacts upon electron transfer with \( \text{H}^* \) under fluoride abstraction, to form \( \text{CF}_2 \text{F}_2 \text{H}_2 \text{OF}^{-} \), which reacts further with \( ^* \text{OH} \) radicals to form \( \text{CF}_2 \text{F}_4 \text{SO}_3^{-} \) and water. We note that \( \text{H}^* \) radicals only exist under anaerobic conditions (Fig. 6). In mechanism II, the intermediate \( \text{CF}_2 \text{F}_4 \text{SO}_3^{-} \) reacts with \( ^* \text{OH} \) radicals, undergoes hydrolysis and decarboxylation reactions, to form \( \text{CF}_2 \text{F}_3 \text{SO}_3^{-} \) upon liberation of CO\(_2^{-}\), whose
A spectroscopic signature is known, and the cycle repeats seven times until only CO₂, HF, and SO₃ remain of PFOS. In contrast, in mechanism III, the intermediate C₁₅F₂₆SO₃⁻ undergoes an H/F exchange and a decarboxylation reaction to form C₁₅F₁₅OH, which is an intermediate of aqueous electrocatalytic PFOA degradation (Fig. 7A). In mechanism III, PFOS-derived C₁₅F₁₅ has been reported to decompose along the oxygen mechanism pathway of PFOA until CO₂ and HF are obtained as final products (Fig. 7B). Likewise, C₁₅F₁₅ decomposition can also proceed through the PFOA hydroxyl radical mechanism to arrive at the desired products CO₂ and HF.

Carbon-based radicals are longer-lived than oxygen-based radicals in aqueous electrolyte, carbon-based radicals are at PFAS molecules, and oxygen-based radicals are the reactive oxygen species that stem from electrolytes. The protonation state, which depends on electrolyte pH and pKₐ values of reactants and intermediates (see Table 4), critically affects mechanistic pathways. For example, the C₁₅F₁₅OH intermediate of the hydrogen peroxide and hydroxyl radical mechanisms in Fig. 7A can only be formed at pH values below 2 (see Table 4).

**Future research directions**

More research is needed to develop viable, globally scalable technologies for the destruction of halogenated organic water pollutants. Systems must work in aqueous media, consist of nonprecious materials, minimize capital expenditures and energy requirements, and be capable of being powered by renewable electricity for sustainability. A quantitative mechanistic understanding of organohalogen destruction via aqueous advanced redox processes is urgently needed, for which analytical detection methods for organohalogens and transient species must be improved, and the development of new catalysts and processes must be advanced.

**Analytical PFAS detection methods**

Detection of low concentrations of organohalogens in the ppb to ppt range is challenging, particularly in natural water samples, in which ubiquitous abundant ions, such as chloride, can interfere. Defluorination performance is typically assessed by fluoride ion quantification by ion selective electrode measurements. Nuclear magnetic resonance (NMR) spectroscopy has been used since the early 1960s to detect PFOA and PFOS, with a limit of detection of 1.5 μM at that time. Gas chromatography (GC) and liquid chromatography (LC) have gradually gained more importance as separation techniques prior to compound identification and quantification. GC can only separate neutral and volatile analytes with low molecular weight, and is limited by low sensitivity and long separation times. Compared to GC, LC is more widely utilized in quantitative organohalogen analysis, owing to its...
ability to separate semi- or non-volatile, polar, higher molecular weight, and thermally unstable compounds.\textsuperscript{47} A widely used analysis technique is LC coupled with mass spectrometry (LC-MS) to detect halogenated contaminants.\textsuperscript{425} which is often used together with reference standards that are currently available for one hundred of the hundreds of potentially relevant PFAS that are harmful to human health.\textsuperscript{426} High-resolution mass spectrometry (HRMS) has emerged as a key tool for identifying legacy and novel PFAS. HRMS can detect more than 750 PFAS.\textsuperscript{427} LC and GC, coupled with various HRMS-based techniques, have been widely used for the identification and quantification of organohalogens.\textsuperscript{428} LC/GC-HRMS has extremely high selectivity, high resolving power, and is capable of detecting unknown PFAS. The lowest limit of PFAS detection for LC/GC-HRMS that has been reported was 100 nM.\textsuperscript{429} The high cost of HRMS instrumentation and challenges with respect to differentiation of PFAS isomers are the main disadvantages of LC/GC-HRMS.\textsuperscript{26} PFAS concentrations down to 10 nM are detectable by mobility spectrometry combined with LC and MS, which provides high selectivity and sensitivity as well as fast detection, but is expensive and unable to distinguish PFAS isomers, which limits broad usability.\textsuperscript{430}

**Catalyst development**

The development of new, nonprecious, efficient, selective, and robust catalysts is critical for the advancement of halogenated pollutant destruction. Catalyst materials are the foundation of degradation technologies because catalysts lower kinetic barriers in the conversion of supplied energy into chemical energy that initiates the degradation process. New synthetic and computational methods are needed to advance the design of robust, active, selective, and globally scalable catalysts, predicated on a quantitative mechanistic understanding.\textsuperscript{6,16,17,305,306,431-435} Advanced \textit{operando} spectroscopies are essential to reveal the electronic and physical structures of catalysts under turnover, which together with catalyst property-performance relationships will accelerate catalyst discovery through rational design.\textsuperscript{435-441} Understanding how surface species bind to catalysts through first principles and machine learning computations is key to inform and direct experimental investigations in the vast materials space.\textsuperscript{442,443}

The electronic and geometric structure of catalysts, including changes during turnover and bonding motifs of reaction intermediates can be determined by advanced \textit{in situ} or \textit{operando} spectroscopies, combined with first principles and machine learning. \textit{In situ} techniques monitor changes of the catalyst material under turnover, whereas \textit{operando} spectroscopies additionally identify and quantify generated products during catalysis, thus enabling direct catalyst property-performance relationships during catalytic cycling. \textit{In situ} and \textit{operando} spectroscopies are often employed to gain a mechanistic understanding of electron, ion, and mass transport at catalyst interfaces,\textsuperscript{444} providing insights into the surface and bulk structure of catalysts, their composition, oxidation states, and adsorbed intermediates under reaction conditions.\textsuperscript{436,441,445}

\textit{In situ} and \textit{operando} spectroscopies additionally enable critical insights into reaction pathways,\textsuperscript{446} especially when coupled with computational studies.

Some of the most frequently used \textit{in situ} and \textit{operando} characterization techniques of catalyst materials are \textit{in situ} Raman and surface enhanced Raman spectroscopy (SERS),\textsuperscript{445,447} Fourier transform infrared spectroscopy (FTIR),\textsuperscript{446} and the synchrotron-based techniques X-ray diffraction,\textsuperscript{446} X-ray absorption spectroscopy,\textsuperscript{448} near ambient pressure X-ray photoelectron spectroscopy,\textsuperscript{446} high-energy-resolution fluorescence-detection X-ray absorption spectroscopy,\textsuperscript{449} and X-ray absorption fine structure spectroscopy,\textsuperscript{449} sometimes used in grazing incidence angle configuration to enhance catalyst surface specific information.\textsuperscript{450} To gain a more accurate and quantitative understanding of catalysts and to reveal critical insights into the thermodynamics and kinetics of species during electrocatalysis, theoretical approaches, such as first principles density functional theory (DFT) calculations and microkinetic modelling simulations are often combined with \textit{in situ} and \textit{operando} characterization techniques.\textsuperscript{436,444,451,452} First-principles calculations, rooted in quantum mechanical electronic structure theory, have been utilized to analyse the interplay between the microscopic processes and the meso- to macroscopic environment.\textsuperscript{453} DFT is the most commonly used first-principle method and utilizes functionals of spatially dependent electron density calculations to investigate the electronic structure of atoms, molecules, and solids.\textsuperscript{454} First-principle calculations are especially important in the context of catalyst discovery because they enable screening for new catalysts based on user-defined criteria and hypotheses, such as optimal activity, stability of elements under specific conditions, formation energy, selectivity, and material phases.\textsuperscript{2,435} These computational screening tools have been employed to analyze ensemble effects and electronic effects, to determine catalytic activity and selectivity.\textsuperscript{455} Electronic effects control the binding of the reaction intermediates.\textsuperscript{455} DFT calculations can be used to predictively design advanced catalysts, utilizing functional mechanisms of existing catalysts, comparing them, and making predictions which of these mechanisms is most suitable for each future reaction.\textsuperscript{442,455} Theoretical predictions from first-principle calculations are based on properties calculated from basic physical quantities and do not consider experimental results. Thus, it is challenging to quantitatively understand catalysts by advanced \textit{in situ} or \textit{operando} spectroscopies or theoretical models alone. Therefore, experimental results and theoretical models are nowadays often combined with machine learning algorithms that enable a better understanding of the nature of chemical bonding and its variation in strength across physically tuneable factors.\textsuperscript{462} Data-driven artificial intelligence models are capable of being integrated into active and iterative learning schemes that incorporate experimental results to improve the extrapolative, \textit{i.e.}, predictive, capabilities of models.\textsuperscript{456,457} Machine learning can also be combined with multi-scale simulations and quantum mechanics to predict the performance of surface sites of catalysts.\textsuperscript{458}

Advanced \textit{in situ} or \textit{operando} spectroscopies, together with computational first principles and machine learning
approaches enable much-needed quantitative understanding of catalytically active sites, reactions centres, and reaction mechanisms.\textsuperscript{446,451,458,459} Right now, detailed DFT calculations and machine learning studies have challenges, such as high computational cost and potential loss of physical intuition since most models consist of complicated mathematical formulations that are difficult to interpret.\textsuperscript{442} Furthermore, reporting of experimental and computational information in much detail must be ensured to overcome challenges regarding choosing suitable functionals in DFT calculations.\textsuperscript{460,461} Multi-disciplinary approaches that combine experimental electrochemical performance assessments, \textit{operando} spectroscopies, and computational approaches have to date the greatest potential to advance catalyst development.\textsuperscript{451}

**Process development**

The thermodynamics, kinetics, mass transport, and chemistries of a system (i.e. the four pillars of chemical engineering) govern the overall electrocatalysis process and are tunable by the electrocatalytic process parameters outlined in Fig. 8. The electrolyte pH critically affects the thermodynamic potentials and chemistries, including generation mechanisms and protonation states, of reactive species produced during catalytic turnover (see Table 3). Electrolytes composed of small ions enhance mass transport, and electrolyte composition affects chemistries, particularly with respect to auxiliary solutes that can form transient radicals with high oxidation or reduction strengths. The electrolyte temperature impacts kinetics and mass transport of the system. The reaction time influences reaction kinetics, and electrolyte agitation increases mass transport. The applied potential controls the thermodynamics, kinetics, and chemistries by making different mechanistic pathways accessible.

The scaleup of halogenated pollutant destruction technologies from the laboratory scale to industrially relevant scales demands that investigated systems are operated in water at pollutant concentrations that occur in the field, or at least at concentrations that are achievable by separation techniques,\textsuperscript{462,463} necessitating optimization of substrate mass transport.

**Detection of transient ARP and AOP species**

Quantitative analytical techniques are needed for the detection of short-lived, highly reactive redox species\textsuperscript{352,464–466} that are produced during assisted or unassisted electrocatalytic ARPs and AOPs, to develop a quantitative mechanistic understanding of organohalogen destruction processes. Electron paramagnetic resonance (EPR) spectroscopy is the premier method for radical detection.\textsuperscript{467–469} Freeze or spin trapping preserves radical species long enough to detect them in an EPR spectrometer.\textsuperscript{435} Spin traps are chemicals that react with radicals to create longer-lived, paramagnetic, EPR-active species, which are used to identify radicals with short lifetimes.\textsuperscript{335} Qualitative radical identification is important for understanding which species are involved in ARP and AOP mechanisms. Nevertheless, quantification is necessary to deeply understand mechanisms, and optimize reaction conditions and overall pollutant degradation. While EPR is typically used for identification of radical species, an external standard, such as 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO), can be utilized to obtain quantitative data.\textsuperscript{470} Other quantitative detection methods are fluorescence and optical spectroscopy that utilize turn-on or turn-off dyes to determine radical concentrations.\textsuperscript{352,471,472} These dyes typically react directly with radical intermediates, resulting in a change in the fluorescence or absorption spectrum of that dye, enabling the determination of concentrations of radical intermediates. Faster, more cost-effective, and more sensitive detection methods must be developed to accelerate the innovation of viable aqueous electrocatalytic organohalogen destruction techniques.

**Conclusions**

Halogenated organic compounds are widespread due to their exceptional utility and because they were initially considered nonmetabolizable and nontoxic, owing to the extreme stability of carbon–halogen bonds. However, prolonged use has led to their accumulation in the environment and organisms globally. We have introduced various classes of these pollutants categorized by halogen type (fluorine, chlorine, bromine), discussed important policies and regulations, outlined their applications, and highlighted associated environmental and human health risks. We discussed remediation techniques, focusing on carbon–halogen bond strengths, capital expense and energy needs for destruction, and electrocatalytic aqueous advanced redox processes. We highlighted mechanistic details of electrolysis, including oxidations and reductions of the water–oxygen system, as well as thermodynamic potentials, protonation states, and lifetimes of radicals and reactive oxygen species in aqueous electrolytes, importantly, at different pH conditions.
We pointed out that advanced reduction processes necessitate anaerobic conditions, which are impractical beyond the laboratory scale because electrocatalytic water oxidation can produce dioxygen, membranes partitioning oxidation and reduction half-reactions cannot completely prevent oxygen crossover, and airtight seals are inherently challenging in large-scale applications; ergo, advanced oxidation processes appear to be more promising. We reviewed aqueous advanced redox processes for different halogenated compounds and PFAS (per- and polyfluoroalkyl substances), detailing potential mechanisms. Future research directions require quantitative understanding of destruction mechanisms, improved detection methods, advanced catalyst development, and energy-efficient processes. Scalable systems using nonprecious materials, powered by renewable electricity, are crucial. We outlined the interconnectedness of electrocatalytic process parameters and their effect on the chemical engineering descriptors thermodynamics, kinetics, mass transport, and chemistries, all vital in steering complex reaction networks. Finally, we suggested strategies to accelerate the development of effective aqueous electrocatalytic techniques for organohalogen destruction.

**Abbreviations**

ACGIH  American Conference of Governmental Industrial Hygienists  
AOP  Advanced oxidation process  
ARP  Advanced reduction process  
BDD  Boron-doped diamond  
BDE-15  4,4’-Dibromodiphenyl ether  
BDE-207  2,2’,3,3’,4,4’,5,6,6’-Nonabromodiphenyl ether  
BDE-22  2,3,4,4’-Tribromodiphenyl ether  
BDE-28  2,4,4’-Tribromodiphenyl ether  
BDE-3  4-Monobromodiphenyl ether  
BDE-47  2,2’,4,4’-Tetraminodiphenyl ether  
BFR  Brominated flame retardant  
CFC  Chlorofluorocarbon  
CFC-11  Trichlorofluoromethane  
CFC-12  Dichlorofluoromethane  
CFC-13  Chlorofluoromethane  
CIPAH  Chlorinated polycyclic aromatic hydrocarbon  
DCE  1,2-Dichloroethane  
decaBDE  Decabromodiphenyl ether  
DFT  Density functional theory  
DMSO  Dimethyl sulfoxide  
e-waste  electronic waste  
EPR  Electron paramagnetic resonance  
Freon-11  Trichlorofluoromethane  
Freon-12  Dichlorofluoromethane  
Freon-13  Chlorofluoromethane  
Fs  Furans  
FTIR  Fourier transform infrared spectroscopy  
GC  Gas chromatography  
GenX  Hexafluoropropylene oxide dimer acid  
HBCD  Hexabromocyclododecane  
HCFC  Hydrochlorofluorocarbon  
HCFC-141b  1,1-Dichloro-1-fluoroethane  
HCFC-142b  Chloro-1,1-difluoroethane  
HCFC-22  Chlorofluoromethane  
HFC  Hydrofluorocarbon  
HRMS  High-resolution mass spectrometry  
LC  Liquid chromatography  
MS  Mass spectrometry  
NMR  Nuclear magnetic resonance  
octaBDE  Octabromodiphenyl ether  
PBB  Polybrominated biphenyl  
PBDD  Polybrominated dibenzo-p-dioxins  
PBDE  Polybrominated diphenyl ethers  
PCB  Polychlorinated biphenyls  
PCB-47  2,2’,4,4’-Tetrachlorobiphenyl  
PCB-77  1,2-Dichloro-4-(3,4-dichlorophenyl)benzene  
PCDD  Polychlorinated dibenzo-p-dioxins  
PCDF  Polychlorinated dibenzofuran  
PCE  Perchloroethylene = tetrachloroethene  
PCET  Proton-coupled electron transfer  
pentaBDE  Pentabromodiphenyl ether  
PERC  Tetrachloroethene  
PFAS  Per- and polyfluoroalkyl substances  
PFBA  Perfluorobutanoic acid  
PFDA  Perfluorodecanoic acid  
PFHxA  Perfluorohexanoic acid  
PFOA  Perfluorooctanoic acid  
PFOS  Perfluorooctane sulfonic acid  
PHB  Poly-β-hydroxybutyrate  
ppb  Parts per billion (μg L⁻¹)  
ppm  Parts per million (mg L⁻¹)  
ppq  Parts per quadrillion (pg L⁻¹)  
pt  Parts per trillion (ng L⁻¹)  
R-11  Trichlorofluoro)methane  
R-12  Dichloro((fluoro)methane  
R-13  Chloro((fluoro)methane  
SERS  Surface-enhanced Raman spectroscopy  
TBBPA  Tetrabromobisphenol-A  
TBP  2,4,6-Tribromophenol  
2,3,7,8-TCDD  2,3,7,8-Tetrachlorodibenzodioxin  
TCE  Trichloroethene  
TEMO  2,2,6,6-Tetramethylpiperidine-1-oxyl  
TLV  Threshold limit value  
TWA  Time-weighted average  
UV  Ultraviolet  
VC  Vinyl chloride  
VUV  Vacuum ultraviolet

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Madeleine K. Wilsey, writing – original draft preparation, writing – review and editing, visualization; Teona Taseska, writing – original draft preparation, visualization; Ziyi Meng, writing – original draft preparation; Wanqing Yu, writing – original draft preparation; Astrid M. Müller, conceptualization, writing – original draft preparation.
preparation, writing – review and editing, visualization, supervision, project administration, funding acquisition.

**Conflicts of interest**

There are no conflicts to declare.

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**Notes and references**
